Materials Genome Initiative (MGI) Sixth Principal Investigator Workshop

July 30-31, 2024
Johns Hopkins University

Welcome to the 2024 Materials Genome Initiative Principal Investigators Workshop!

This draft of the meeting booklet contains abstracts for the 130 PI posters presented during the two-day meeting. A final version of the booklet will be published on the website in the middle of August with summaries and reports from the workshop breakout sessions and panel discussions. Poster presenters will find the location of the poster on their nametag and in the meeting Whova app. Attendees can find all the abstracts and the poster locations in the mobile of online version of the app.

The Materials Genome Initiative (MGI) was launched in 2011 to accelerate the discovery, design, development, and deployment of new materials, at a fraction of the cost, by harnessing the power of data and computational tools in concert with experiment. The interagency initiative includes broad participation, including the National Science Foundation (NSF), the Department of Energy (DOE), the Air Force Research Laboratory (AFRL), the Office of Naval Research (ONR), the U. S. Army Combat Capabilities Development Command (DEVCOM), and the National Institute of Standards and Technology (NIST). 2024 marks the sixth time funding agencies, the OSTP Subcommittee for the MGI (SMGI), and Principal Investigators from across the research spectrum have convened to provide and assessment of the status of the initiative and provide a springboard to collaborative work leveraging rapid growth in data, data-driven, AI/ML, and community-wide infrastructure development.

In 2024, MGI PI workshop was hosted by Johns Hopkins University in the Bloomberg Center at 555 Pennsylvania Avenue, Washington, DC and addressed the MGI mandate to biennially assess and report on progress; incorporate input from the interagency SMGI Advisory Board; create engagement of PIs; and deepen the national materials data network manifest in the Materials Research Data Alliance (MaRDA) as called out in the current MGI Strategic Plan. The workshop program included reports and panel discussions of national priorities, recent program evaluations, aligned international efforts, and new directions for AI and autonomous materials discovery. Current MGI investigators presented 130 posters and provide brief oral presentations of a dozen projects provided supplemental funding to pursue outcomes of the 2022 PI workshop. Convening in Washington resulted in record attendance both by PIs and by representatives of the agencies engaged in the MGI. A central goal of the meeting was to engage attendees in evaluation of MGI roles in societal-level challenges to both survey existing resources and identify important gaps and barriers that can focus development of the materials innovation infrastructure central to accelerated, data and AI driven materials discovery, design, and deployment.

The final version of this book will include summaries and report outs of workshop activities. This draft contains abstracts from the 130 posters presented by investigators across the MGI. Draft organization is alphabetical by PI last name. Poster locations can be found in the meeting app and online sites.

Acknowledgements: The MGI PI meeting is supported by NSF Award 2422384 (Nguyen and Elbert). JHU Organizing Committee: David Elbert (HEMI), Todd Hufnagel (DMSE), Vicky Nguyen (DME), Sarah Preis, Chris Pottillo, Dina King, Salena Fitzgerald, Tracy Marshall, Steven Ransom. Student Assistants: Liz Chua (JHU), Naman Parikh (CMU), Spencer Leach (Va Tech), Gannon Murray (Earlham), Sebastian Grabill (Calvin), Jordan Bass (NSF), Harrison Park (JHU), and Jeevan Dalip (JHU).

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DMREF: Deep learning guided twistronics for self-assembled quantum optoelectronics

Lead Investigator: Ritesh Agarwal, riteshag@seas.upenn.edu
Participating Institutions: University of Pennsylvania, University of Wisconsin at Madison, Northeastern University
Source of Support: NSF-DMREF
Website: None
Keywords: supertwisted, spiral, quantum optoelectronics, twistronics, deep learning.

Project Scope

In this project, we will break the fundamental limitation of designing twistronic materials via deep-learning based symmetry and topological engineering of materials and metamaterials. We will start from a quantum paradigm to optimize the atomic scale symmetry and topology in 2D materials for prescribed chiral responses. Guided by theory, novel and rational synthesis will enable direct growth of 2D materials with control over interlayer twist angles, compositions, and crystal phases to realize novel and predictable quantum properties. New knowledge will be generated that can enable the design of highly engineered quantum materials with new degrees of freedom with high predictive power to demonstration of novel chiral optoelectronic responses. Understanding of the symmetry-topology-response relationships will lead to designs of new photonic metamaterial platforms with novel chiral responses to structured light to produce desired complex optical response from the material system with patterned external fields.

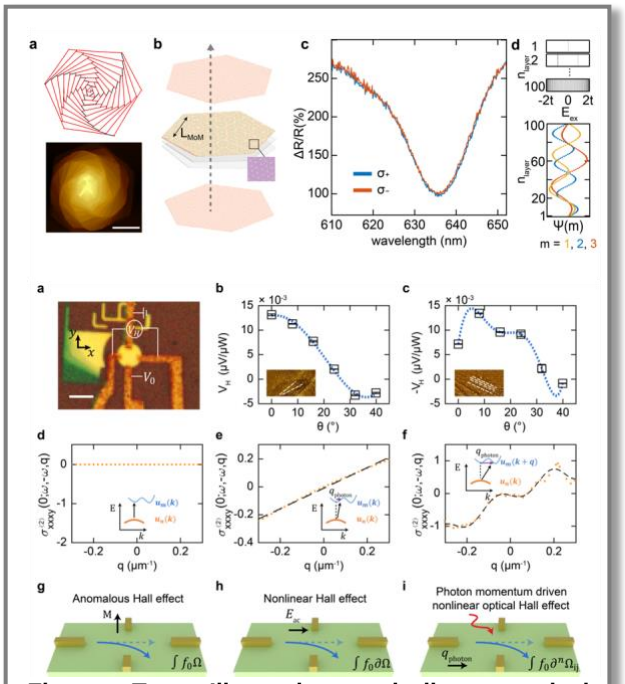


Figure. Top: Illustration and linear optical characterization of the 3D chiral systems from supertwisted spirals of WS_2. Bottom: Opto-twistronic Hall response from spiral lattice-photon momentum interactions.

Relevance to MGI

The emergence of twisted quantum material systems opens a vast and diverse material space for materials discovery and design. The advance of artificial intelligence (AI) in the fields of graph theory, equivariant neural network, and nature language processing, offers an essential toolbox – when combined with domain knowledge and other data-driven approaches – to aid both materials discovery and device design in every single aspect. Motivated by the MGI, we will develop state-of-the-art data-driven approaches and computational methods to guide and accelerate the material discovery and device development cycle. A twisted 2D materials database will be created by high-throughput computation based on newly developed methods for large-scale systems and GPU-based computation. Thereafter, deep learning based on Wannier functions and Hamiltonian-centric graph neural networks will be constructed to learn and discover the "materials genome" from a vast material design space and accelerate the inverse design of novel quantum phases in multilayered twisted materials and further extend it to photonics.

Technical Progress

In the first year of the project, a major achievement is the observation of the nonlinear optical Hall effect in self-assembled supertwisted multilayered (>5-100 nm thickness) WS_2 system formed by a screw-dislocation-driven mechanism. The optical Hall current direction changed with the structural handedness of the supertwisted system, along with an unusual photon-momentum dependence of the nonlinear optical response in the moire potential. Signatures of thickness-dependent exciton-polaritons and the associated strong photon momentum-lattice

interaction dependent photocurrent response were measured, which suggest a fundamentally altered light-matter interaction in 3D Moire systems. Our study seamlessly connects 2D and 3D twistronics and provides a bridge connecting the electrons and photons by overcoming their significant length scale differences in conventional systems.

We also developed a physics-informed neural network approach bridging deep-learning force field and electronic structure simulations, illustrated through twisted large-scale MoS_2 systems. Using the Wannier functions as the basis, we categorize the Hamiltonian elements based on physical principles to incorporate diverse information from a deep-learning force field model. This Wannier-based dual-functional model for simulating electronic band and structural relaxation (WANDER) serves as a powerful tool to explore large-scale supertwisted systems in the future.

Future Plans

Combining experiment, computation, and theory, we will explore novel phenomena induced by superspiral structures (such as chiraloptical effect) in multilayered twisted MX_2 systems. We will synthesis and explore supertwisted quantum material systems beyond transition metal dichalcogenides guided by data-driven approaches. Utilizing Wannier functions as the basis, we will endow new capabilities to the ML model to predict novel properties associated with supertwisted MX_2 systems, such as Berry curvature, density of states, and other topological properties. We will develop unique photonic structures for the demonstration of new quantum optoelectronic functionalities in high-dimensional quantum entanglement generation and flat-band cavity-quantum electrodynamics for efficient chiral light emission and detection.

Broader Impacts and Workforce Development

At the core of this DMREF proposal is to design and obtain a deeper understanding of topological quantum and photonic materials by combining elements of empirical knowledge, condensed matter theory and deep learning and data mining techniques. These designer twistronics materials with new twist degree of freedom will host novel phenomena that will also enable us to understand excitations in topological quantum materials by experimentally seeking for responses with novel features that describe these interactions. If successful, the proposed materials discovery with unique chiral optoelectronic responses can enable the next generation of electronics and optical devices (e.g. quantum switches, high-dimensional quantum entanglement, chiral emitters and detectors) where their response can be precisely controlled. The interdisciplinary nature of this research program will also provide an excellent educational opportunity for training the next generation of graduate and undergraduate students. The main goals of our educational and outreach program are to: a) enhance our undergraduate and graduate courses, b) improve the participation of undergraduates in cutting-edge research, and c) outreach and inclusion of underrepresented groups.

Data Management and Open Access

The datasets for training the ML model developed in the first year are available at the Digital Repository Service of Northeastern University (http://hdl.handle.net/2047/D20630194). The code for the work is available on GitHub (http://github.com/yuboqiuab/multifunctional). We will continue to make sure that all the data practices associated with publications are consistent with the FAIR standard.

Advancing Along the Materials Development Continuum and Partnerships to Translation

An open-access database including both twisted and supertwisted two-dimensional material systems will be constructed and shared with the public with a web interface.

Publications and References

1. Z. Ji, Y. Zhao, Y. Chen, Z. Zhu, Y. Wang, W. Liu, G. Modi, E. J. Mele, S. Jin, R. Agarwal, “Opto-twistronic Hall effect in a three-dimensional spiral lattice”, arXiv:2312.10954. DOI: 10.48550/arXiv.2312.10954

2. Y. Qi, W. Gong, Q. Yan, “Bridging deep learning force fields and electronic structures with a physics-informed approach”, arXiv:2403.13675. DOI: 10.48550/arXiv.2403.13675

Low Cost, High Strength and Ductile Mg Alloys

Lead Investigator: Sean R. Agnew, agnew@virginia.edu
Participating Institutions: University of Virginia, Cornell University, University of Canterbury
Source of Support: NSF-DMREF
Website: none.
Keywords: Lightweight, Alloy design, Precipitation, GP zones, Crystal plasticity.

Project Scope

As the lightest structural metals, Mg alloys provide unique opportunities to enhance energy efficiency in the transportation sector. Nevertheless, wrought Mg alloys remain underutilized, due to high processing costs and inadequate mechanical properties. This project aims to simultaneously improve strength and ductility, while being cognizant of cost. The new materials design strategy utilizes GP-zones composed of elements widely available in the earth's crust (e.g., Mg, Al, Ca). It is hypothesized that the thermally activated dislocation-GP-zone interactions increase strain rate sensitivity, leading to improved ductility, in addition to the obvious strengthening effect.

Relevance to MGI

This project combines computational and experimental techniques from atomic length scales to the macroscale (**Figure 1**). Given the macroscopic stress-strain response and the microstructure, the single crystal strength and strain hardening parameters can be inferred from crystal plasticity simulations. This "top-down" approach relates the macroscale mechanical properties to dislocation-precipitate interactions within individual crystals. The "bottom up" approach involves prediction of precipitate structures and fundamental physical parameters such as coherency strain due to lattice mismatch, stacking fault energies, and elastic moduli using density functional theory (DFT) and statistical mechanics-based mixed-space cluster expansion models. Together, the single crystal strength can be obtained from first principles and compared with the ones obtained from crystal plasticity simulations. Once validated, this comprehensive solution to the forward modeling problem provides the basis for the inverse problem represented by goal-driven materials design.

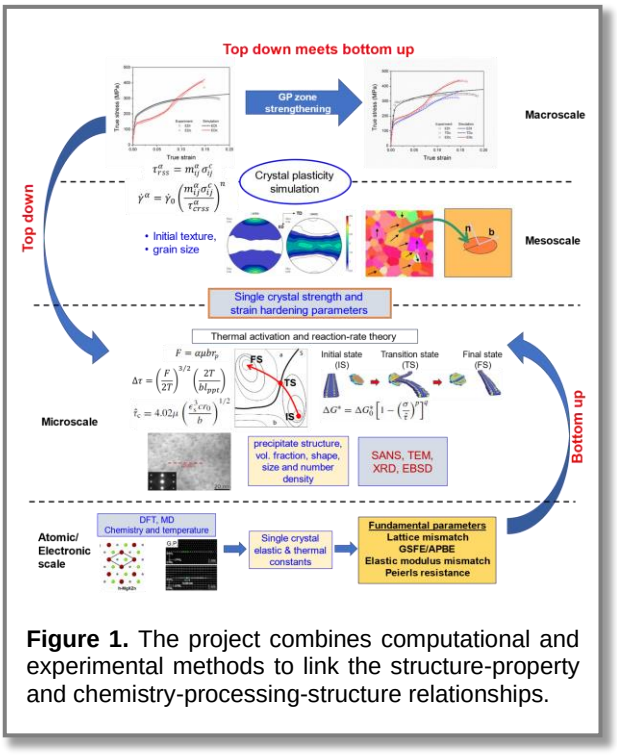


Figure 1. The project combines computational and experimental methods to link the structure-property and chemistry-processing-structure relationships.

Technical Progress

Atomic structures of ordered monolayer Guinier-Preston (GP) zones in Mg-Zn-X (X = Ca, Nd)[1]and Mg-Al-Ca[2] systems have been predicted based on first-principles calculations combined with the statistical-mechanical approach of cluster expansion (CE). Advanced TEM/STEM imaging techniques have provided atomic resolution imaging with atomic number contrast. Simulated TEM images and diffraction patterns of the predicted structures agree well with prior experimental observations. Notably, the determined structure is distinct from the one which was proposed and remained uncontested in the literature for nearly two decades.

Comprehensive first-principles calculations based on DFT, CE and Monte Carlo (MC) simulations are being performed to study the crystal structures and stabilities of phases in Mg-Zn system, including GP zones, β_1', β_2' and stable β phase[3,4]. Mixed-space cluster expansion (MSCE) is generalized to systems with arbitrary crystal symmetry and multiple sublattices by formulating compatible reciprocal space interactions and developing a crystal-symmetry-agnostic algorithm for the calculation of constituent strain energy[5]. A neural network-based approach to describe the interatomic potential of Mg-Zn-Ca is near completion, and the process has already enabled predictions of GP zone stiffness and generalized stacking fault and anti-phase boundary (APB) energies. Furthermore, both experimental and simulation-based results have shown that the evolution from GP zone to metastable precipitate to

equilibrium phase involves enrichment in the more slowly diffusing species, Zn. Precipitation sequence and key precipitate phases of dilute Mg-Zn-Ca alloys were reexamined combining Advanced TEM and DFT[6,7]. Machine learned interatomic potentials have been developed for Mg, Ca, and the binary Mg-Ca system. The interatomic potentials for Zn, Ca-Zn, Mg-Zn, and Ca-Mg-Zn systems have proven more challenging but are required to perform the planned MD simulations of dislocation-GP zone interactions.

The age-hardening response of 4 candidate alloys has been characterized, including 1 in the Mg-Al-Ca-Mn (AXM) and 3 in the Mg-Zn-Ca-Zr (ZXK) quaternary systems. Metallurgical and mechanical property characterization of the 4 alloys in various thermomechanical processing conditions has been performed. The possibility of natural aging and concerns of natural over-aging have been explored, with aging times of up to one year, and no statistically significant difference in the tensile stress strain behavior is observed.

The results of polycrystal plasticity modeling of the observed mechanical responses have helped answer a number of practical and mechanistic questions. First, the approach revealed that crystallographic texture distinctions explain why sheet forms of the alloys are less potently strengthened than extruded product forms.[8] Second, the approach was able to show that the GP zones in both AXM[9] and ZXK[6] alloys impart about 2.5x more strengthening on the prismatic slip systems, as compared to the basal. This is not due to the GP zone shape (which actually impacts basal slip more strongly than prismatic). Rather, it is due to the intrinsic shearing resistance which is far greater for prismatic dislocations because they induce an APB within the GP zone. While these strength differences contribute to the intrinsic plastic anisotropy of Mg alloys, the weak crystallographic texture observed in these sheet alloys, and the positive impact of GP zone strengthening upon the strain rate sensitivity enables the alloys to maintain good ductility even in the peak aged condition[8]. Finally, it has been revealed that material in the as-rolled (work hardened) condition exhibits even higher strength than the peak aged, with acceptable ductility and polycrystal plasticity enables the degree of work hardening to be optimized for a particular strength/ductility combination of interest.

Future Plans

Design criterions for forming prismatic plates in hcp Mg are being explored using computational thermodynamics. The development of neural network-based interatomic potential will enter the training-testing-revising cycle and the parameter will be finalized. The aforementioned interaction between the dislocations and the GP zones, accounting for the coherency strain fields and mismatch between the elastic modulus is being performed using a FFT-based DDD code which can account for shearable obstacles like GP zones[10].

Broader Impacts and Workforce Development

The broader impacts of the project are development of computational tools for the prediction of multicomponent alloy structure and performance and a new paradigm for GP zone-strengthened alloy development. The project is also educating a diverse group of graduate students and postdoctoral fellows including members of underrepresented groups: MEng students, Oluwaniyi Ajiteru (now with Micron Technologies, Manassas, VA) and Aaron Sullivan; PhD students, Du Cheng (Acta Student Award[1], now Postdoctoral Research Associate in Shanghai Jiao Tong University), Yuan-Chen Gao, and Bassel Khoury; Postdocs, Eric Hoglund (now Postdoctoral Research Associate at Oakridge National Lab) and Kang Wang (now associate professor in Shanghai Jiao Tong University); and research scientist, Jishnu Bhattacharyya. Monthly meetings provide the students and postdocs with deep exposure to the collaborative nature of advanced materials development research.

Data Management and Open Access

The developed computational package implementing the MSCE and MC has been made open-source and uploaded to the online platform GitHub (https://github.com/Bi-Cheng/MSCE). The predicted and experimentally verified atomic structures of GP zones and metastable precipitates are uploaded as supplementary materials of publications. The DFT-generated training set for neural network-based atomic potential will be uploaded to online repositories, such as Materials Cloud.

Advancing Along the Materials Development Continuum and Partnerships to Translation

New ternary alloy compositions are being explored using established criterions for forming prismatic plates in hcp Mg alloy matrix. We plan to test the predicted compositions in collaboration with experimental colleagues.

Publications and References

(1) Cheng, D.; Hoglund, E. R.; Wang, K.; Howe, J. M.; Agnew, S. R.; Zhou, B.-C. Atomic Structures of Ordered Monolayer GP Zones in Mg-Zn-X (X= Ca, Nd) Systems. *Scripta Materialia* **2022**, *216*, 114744. https://doi.org/10.1016/j.scriptamat.2022.114744.

(2) Gao, Y.-C.; Zhou, B.-C. Atomic Structures of GP Zones in Mg-Al-Ca Alloys. *in preparation*.

(3) Cheng, D.; Wang, K.; Zhou, B.-C. Crystal Structure and Stability of Phases in Mg-Zn Alloys: A Comprehensive First-Principles Study. *Acta Materialia* **2023**, *242*, 118443. https://doi.org/10.1016/j.actamat.2022.118443.

(4) Cheng, D.; Wang, K.; Zhou, B.-C. First-Principles Investigation of the Early-Stage Precipitations in Mg-Sn and Mg-Zn Alloys. In *Magnesium Technology 2022*; Maier, P., Barela, S., Miller, V. M., Neelameggham, N. R., Eds.; The Minerals, Metals & Materials Series; Springer International Publishing: Cham, **2022**; pp 281–290. https://doi.org/10.1007/978-3-030-92533-8_47.

(5) Wang, K.; Cheng, D.; Zhou, B.-C. Generalization of the Mixed-Space Cluster Expansion Method for Arbitrary Lattices. *npj Comput Mater* **2023**, *9* (1), 75. https://doi.org/10.1038/s41524-023-01029-0.

(6) Bhattacharyya, J.; Faberman, S.; Li, Z.; Sullivan, A.; Du, C.; Khoury, B.; Gao, Y.-C.; Sasaki, T.; Zhou, B.-C.; Warner, D.; Agnew, S. Guinier-Preston (GP) Zone Strengthening of Dilute Magnesium Alloys Comprised of Earth-Abundant Elements. *Submitted to Scripta Materialia*.

(7) Li, Z. H.; Cheng, D.; Wang, K.; Hoglund, E. R.; Howe, J. M.; Zhou, B. C.; Sasaki, T. T.; Ohkubo, T.; Hono, K. Revisited Precipitation Process in Dilute Mg-Ca-Zn Alloys. *Acta Materialia* **2023**, *257*, 119072. https://doi.org/10.1016/j.actamat.2023.119072.

(8) Bhattacharyya, J.; Sasaki, T.; Nakata, T.; Agnew, S. Why Rolled Mg-Al-Ca-Mn Alloys Are Less Responsive to Aging as Compared to the Extruded. *Scripta Materialia* **2023**, *233*, 115513.

(9) Bhattacharyya, J.; Sasaki, T.; Nakata, T.; Hono, K.; Kamado, S.; Agnew, S. Determining the Strength of GP Zones in Mg Alloy AXM10304, Both Parallel and Perpendicular to the Zone. *Acta Materialia* **2019**, *171*, 231–239.

(10) Santos-Güemes, R.; Capolungo, L.; Segurado, J.; LLorca, J. Dislocation Dynamics Prediction of the Strength of Al–Cu Alloys Containing Shearable Þeta″ Precipitates. *Journal of the Mechanics and Physics of Solids* **2021**, *151*, 104375.

Collaborative Research: DMREF: Discovery of Novel Phases Through Pseudospin Control

Lead Investigator: D.F. Agterberg agterber@uwm.edu, L. Li lian.li@mail.wvu.edu, and M. Weinert weinert@uwm.edu
Participating Institutions: University of Wisconsin-Milwaukee, West Virginia University
Source of Support: NSF-DMREF
Website: https://sites.uwm.edu/pseudospin
Keywords: pseudospin, altermagnetism, MBE-STM-ARPES

Project Scope

This project combines analytic and predictive computational theory with experimental molecular beam epitaxy (MBE) growth and characterization with *in situ* scanning tunneling microscopy/spectroscopy (STM/S) and angle-resolved photoemission spectroscopy (ARPES) to control non-spin-1/2 pseudospin fermions in epitaxial materials, where novel phases and materials properties can be achieved by tailoring lattice strain, proximity effects, charge doping, and electrical and optical gating. Specifically, we will use analytic and first principle solutions of interacting electron Hamiltonians to engineer altermagnets, odd-parity multipole magnets, and high-field superconductivity through pseudospin control.

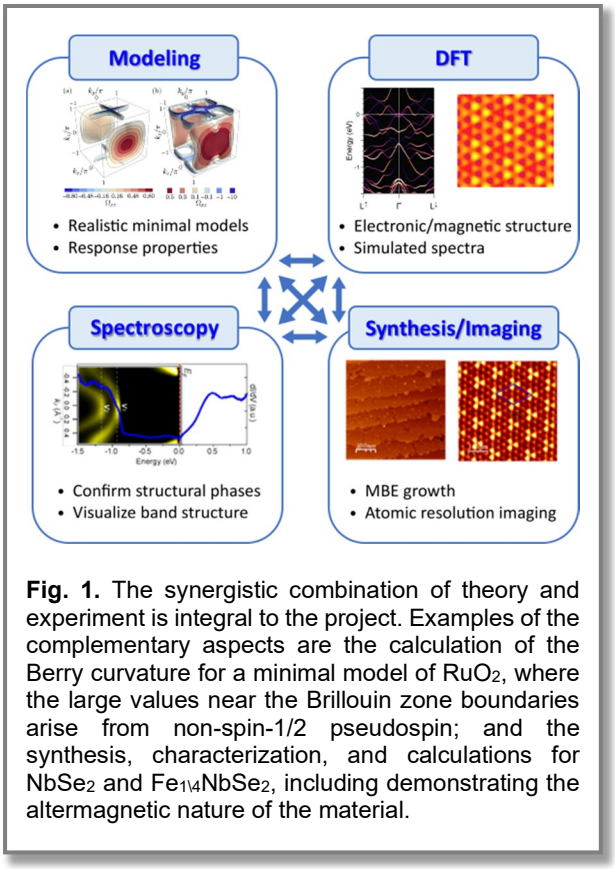


Fig. 1. The synergistic combination of theory and experiment is integral to the project. Examples of the complementary aspects are the calculation of the Berry curvature for a minimal model of RuO_2, where the large values near the Brillouin zone boundaries arise from non-spin-1/2 pseudospin; and the synthesis, characterization, and calculations for $NbSe_2$ and $Fe_{1/4}NbSe_2$, including demonstrating the altermagnetic nature of the material.

Relevance to MGI

To realize the efficient discovery of altermagnetic, odd-parity magnetic, and high-field superconducting materials, we will follow the collaborative and iterative closed-loop approach outlined in the MGI strategic plan. Specifically, we integrate the PIs' strengths and expertise in DFT calculations (Weinert), many-body modeling of phenomena such as superconductivity and magnetism (Agterberg, Weinert), and material synthesis and atomic scale imaging and spectroscopy (Li). The calculations and modeling will help interpret and guide the experimental investigations; at the same time, the experiments will provide data to test the theory and offer important insights into which aspects and parameters of the real materials are important and must be included in the models.

Technical Progress

We have made theory progress in three directions. First is the discovery that the Stoner instability of non-spin-1/2 pseudospin is to a magnetic state very different than ferromagnetism. This Stoner instability leads to magnetic states that break reversal symmetry, have a vanishing magnetization, are non-collinear, and exhibit altermagnetic-like energy band spin-splittings. A second direction has led to a design principle to stabilize altermagnetism in two-dimensional materials. We have found that by tuning to coincident van Hove singularities in five lattice structures that support non-spin-1/2 pseudospin, altermagnetism becomes the dominant electronic instability in the weak-coupling limit. We have also developed a class of minimal models for altermagnetism that encompass forty different

crystal structure types, including monoclinic, orthorhombic, tetragonal, rhombohedral, hexagonal, and cubic materials. These models reveal that non-spin-1/2 pseudospin serves as a design principle for optimizing the Berry curvature in altermagnets and reveal that symmetry-imposed band degeneracies in non-symorphic materials enhance the tendency towards altermagnetism. To connect these models to real systems, we have focused our calculations on $Fe_{1/4}NbS_2$ and $Co_{1/4}NbSe_2$ motivated by our modeling that links the 2a Wyckoff position of Fe/Co in the non-symmorphic space group 194 to an altermagnetic state with a momentum dependent spin splitting of the form $k_yk_z(3k_x^2-k_y^2)$.

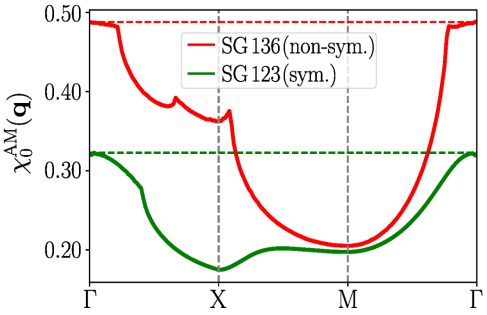


Fig. 2 Design principle based on altermagnetic susceptibility: non-symmorphic materials are more likely to host altermagnetism than symmorphic materials.

As a first step towards the synthesis of transition metal intercalated $NbSe_2$ and NbS_2, we have demonstrated the growth of single-layer 1H-$NbSe_2$ on graphene and $SrTiO_3$ (STO) (001) substrates using MBE. *In situ* ARPES measurements of valence band structures at 77 K reveal that the 1H variant exhibits metallic behavior. STM imaging reveals the well-ordered (3x3) charge density wave on single-layer 1H films, similar to that observed on the surface of bulk 2H-$NbSe_2$. These ARPES and STM results agree with our simulated STM images and the bands (Fig.1).

Future Plans

We will use minimal models and electronic structure calculations to study the relationship between spin-orbit-coupling driven magnetization and the anomalous Hall effect, altermagnetic domain walls, and transport properties such as non-linear Hall and other non-linear transport linked to the non-symmorphic band degeneracy driven quantum geometry. Experimentally, we will synthesize transition metal intercalated $NbSe(S)_2$ and single-layer FeSeS/STO using MBE and compare the STM/STS and ARPES spectra to our calculated altermagnetic properties.

Broader Impacts and Workforce Development

PI Li jointly organized the Unleashing Innovation in Energy Science Workshop: A Journey from First Principles to Data-Driven Autonomy at WVU's Annual Research Week. Newly recruited female graduate student Marzieh Yousefi presented a poster on the MGI approach to synthesizing altermagnets. We have hired three postdoctoral associates: Dr. Yue Yu and Dr. Merce Roig (to start in January 2025) at UWM and Dr. Jiaqi Guan at WVU. We supported graduate students Hao Wu at UWM and Marzieh Yousefi at WVU. Online instructional materials will be posted on our project website, advertised, and highlighted at outreach events such as MGI Day and MGI Summit of STARs.

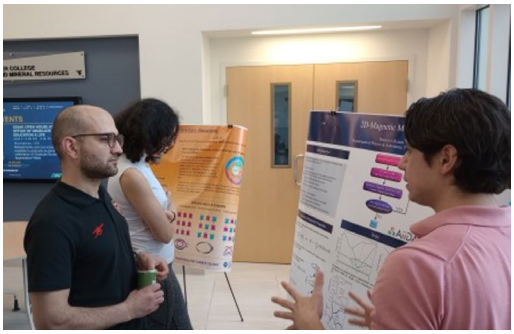


Fig. 3 Graduate student Marzieh Yousefi at the Unleashing Innovation in Energy Science Workshop at WVU's Annual Research Week.

Data Management and Open Access

All publications are publicly available on the arXiv. During this project, the further development of DFT and related analysis codes will be made available to other researchers (via GitHub).

Advancing Along the Materials Development Continuum and Partnerships to Translation

The development of non-spin-1/2 pseudospin control will be a powerful new tool in materials by design, which can lead to large and controllable anomalous Hall effects and new pseudospin-based spintronic materials both of which represent paradigm shifts in materials discovery.

Publications and References

1. Y. Yu, T. Shishidou, S. Sumita, M. Weinert, and D. F. Agterberg, *Spin-orbit enabled unconventional Stoner magnetism*, arXiv:2310.00838 (2023). DOI: https://doi.org/10.48550/arXiv.2310.00838

2. Y. Yu, H.-G. Suh, M. Roig, and D.F. Agterberg, *Altermagnetism from coincident Van Hove singularities: application to κ-Cl*, arXiv:2402.05180 (2024). DOI: https://doi.org/10.48550/arXiv.2402.05180

3. M. Roig, A. Kreisel, Y. Yu, B.M. Andersen, and D.F. Agterberg, *Minimal Models for Altermagnetism,* arXiv:2402.15616 (2024). DOI: https://doi.org/10.48550/arXiv.2402.15616

3D Structures by Block Copolymer Self-Assembly

Lead Investigator: Alfredo Alexander-Katz, aalexand@mit.edu, Caroline A. Ross, caross@mit.edu, collaboration with Vincenzo Vitelli, vitelli@uchicago.edu
Participating Institutions: Massachusetts Institute of Technology, University of Chicago
Source of Support: NSF-DMREF
Website: http://soft-materials.scripts.mit.edu/www/, https://caross.mit.edu/
Keywords: Block Copolymer, Self-Assembly, Dissipative Particle Dynamics, 3D nanofabrication

Project Scope:

This project aims to understand the physics underlying block copolymers to self-assemble into three-dimensional structures in thin films combining experiment and computation. The structure of diblock copolymers such as polystyrene-block-poly(2-vinylpyridine) (PS-b-P2VP) and bottlebrush copolymers such as Polystyrene-branch-Polydimethylsiloxane (PS-branch-PDMS) and Polystyrene-branch-Polydimethylsiloxane-block-Polylactic Acid (PS-branch-PDMS-b-PLA) are studied experimentally and computationally using Dissipative Particle Dynamics (DPD). Our research not only obtains and elucidates the formation mechanisms of intriguing 3D structures, such as multilayer structures and mesh networks, which have great potential in nanofabrication, but also develops and disseminates simulation packages for new block copolymer systems.

Relevance to MGI:

Experimentation and computation have been closely synergized in this project. Simulation has been very helpful in designing and understanding experiments. For example, simulations under various conditions-such as compositions, surface topographies, and interaction parameters-are readily carried out to construct phase diagrams, providing a reasonable starting point for selecting experiment conditions in specific regimes.[1] Additionally, simulations provide mechanistic insights into kinetic pathways to equilibrium structures and molecular chain conformation and stacking.[2,3] The effectiveness of simulation in guiding experiments heavily depends on its accuracy and ability to reproduce experimental results. Therefore, existing experimental results are important training data to verify the parameter and physical mechanisms integrated in the models.[4] By combining experimental and computational approaches, we have gained a better understanding of numerous principles behind designing and preparing 3D structures using diblock and Janus bottlebrush copolymers.

Technical Progress:

Overall, this project explores the principles and strategies for using two types of block copolymer materials to create functional 3D structures.

When diblock copolymer PS-P2VP was submerged in an acidic solution containing metallic compounds, the pyridine groups in P2VP became positively charged by H^+, allowing the anionic metal complex to infiltrate the P2VP block through electrostatic interaction. This infiltration significantly decreased the polymer's mobility, preserving (i.e. locking) the structure during spin coating and annealing of subsequent layers. Furthermore, the infiltrated metal could be exfiltrated using a basic complexing solution, enabling reversible locking and unlocking of self-assembled structures. Utilizing this reversible metal infiltration technique, we could construct 3D multilayer structures with independent control of each layer.[5]

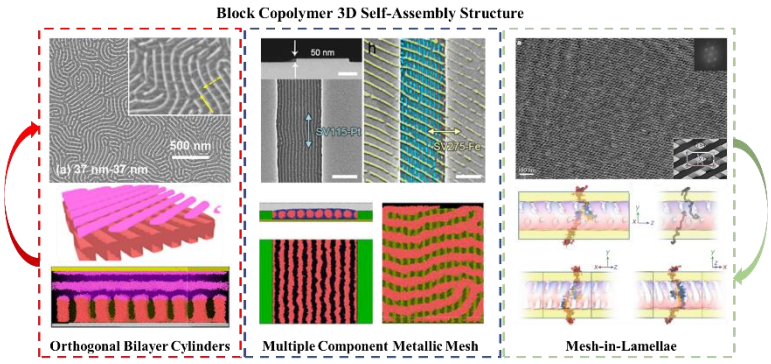


Figure. Block copolymer 3D self-assembly structure study by experiment and DPD: orthogonal bilayer cylinders on bare substrates, orthogonal metal meshes, and hierarchical mesh-in-la-

The selective infiltration of metal ions into P2VP also enables the preparation of multicomponent functional metal nanostructures. In another study on cylindrical forming PS-b-P2VP (SV 115 kg/mol, $f_{P2VP} = 31.7\%$ and SV 275 kg/mol, $f_{P2VP} = 32.7\%$) self-assembly over trenches and mesas, we find that the in-plain cylinders align either parallel or perpendicular to the trench edge, depending on the ratio between film thickness and trench depth. By tracking morphology evolution using DPD, we believe that the parallel orientation

arises from an initial wetting layer on trench walls propagating into the trench, while the perpendicular orientation is due to solvent flow from mesas to trenches during annealing. We prepared bilayers of cylinders, with each layer having a different orientation and different infiltrated metal.[2]

The DPD model, previously used primarily to simulate bulk morphology, had limitations in reproducing thin film morphologies, such as perforated lamellae structures. Therefore, in our simulation-focused papers, we reparameterized the DPD model to accurately reproduce the experimentally observed composition-thin film morphology relation. Additionally, the interaction between polymer and trenches, and post arrays were also optimized to simulate directed self-assembly cases.[4] With the reparameterized DPD model, we simulated stacking layers of A-b-B and A-b-C, hypothesizing that the shared block can transfer morphological information between two layers. By varying film thicknesses, interaction parameters, and compositions, we achieved a rich morphology including meshes and multiple layers of parallel cylinders.[6]

Besides preparing network structures in a layer-by-layer fashion, we also investigated mesh-forming Triblock Janus Bottlebrush Copolymers (TJBBCP) PS-branch-PDMS-b-PLA ($PDMS_{5\ kg/mol}$-branch-$PS_{6.9\ kg/mol})_{30}$-b-$(PLA_{6.3\ kg/mol})_{30}$. The TJBBCP formed a hierarchical structure, where the PLA formed a lamellae superstructure and the PS-branch-PDMS forms a substructure confined within the PLA lamellae. For the substructure, we observed a unique M^{15} mesh network for the first time in literature. Using DPD simulation to visualize chain arrangement and comparing with diblock Janus bottlebrush copolymers, we found that the intrinsic molecular confinement exerted by the PLA superstructure is responsible for the unique mesh network[1,3]. Moreover, the bottlebrush architecture allowed for adjustments in molecular weight and brush number in each block, providing independent control over the morphology type and scale size of the super and substructure[7].

Future Plans:

We plan to experimentally investigate the self-assembly structure of TJBBCP when directed with geometrical patterns, such as trenches, square arrays, and circle arrays. DPD simulation will also be applied to understand how the super and substructure respond to geometrical confinements. The project aims not only to address the fundamental question of how TJBBCP stack under complex spatial confinements and their resulting structures, but also to improve the long-range order of the mesh network to enhance their potential for applications and develop computational methods to explain and predict the morphologies, with implications for nanoscale fabrication. By modeling the effect of solvent annealing and metal infiltration/exfiltration on polymer conformation and morphology, we will develop predictive processing models for polymer-based nanofabrication.

Broader Impacts and Workforce Development:

Four graduate students and one postdoc participated in the project, acquiring skills in polymer thin film processing, characterization, thin film patterning, and DPD simulation. They have attended and will attend multiple high-impact research conferences to present the results listed above, including the 2024 APS and 2024 ACS meetings. Usually a supercloud server is needed to complete the DPD simulation within a reasonable amount of time. To assist researchers unfamiliar with the supercloud interface, we have posted detailed instructions on GitHub on how to apply for an account and submit computation jobs through command lines.

Data Management and Open Access:

We are devoted to sharing our data and code in the belief that it will help others with their research. In our study of TJBBCP (doi.org/10.1038/s41565-022-01293-z), the DPD simulation was conducted using software LAMMPS. The code to generate initial files for LAMMPS, as well as the post-processing scripts, are available as open-source on GitHub.

Advancing Along the Materials Development Continuum and Partnerships to Translation:

To apply block copolymer self-assembly structures to lithographic applications, significant efforts have been devoted to eliminating undesired defects. These efforts, involving chemoepitaxy and graphoepitaxy, are often time-consuming. As a result, block copolymers can be more readily applied in scenarios where performance is more tolerant to minor structural defects, such as organic photovoltaics. We have submitted a proposal for synthesizing donor-block-acceptor block copolymer and optimizing their structure to improve the organic solar cell performance and long-term stability.

Reference:

1 R. Liu, H. Huang, Z. Sun, A. Alexander-Katz, and C. A. Ross, *Experimental and Computational Evaluation of Self-Assembled Morphologies in Diblock Janus Bottlebrush Copolymers*. Nano Lett **23**, 177-182 (2023). doi:10.1021/acs.nanolett.2c03927

2 R. Liu, H. Huang, Z. Sun, A. Alexander-Katz, and C. A. Ross, *Metallic Nanomeshes Fabricated by Multimechanism Directed Self-Assembly.* ACS Nano **15**, 16266-16276 (2021). doi:10.1021/acsnano.1c05315

3 Z. Sun, R. Liu, Su. T, H. Huang, K. Kawamoto, R. Liang, B. Liu, M. Zhong, A. Alexander-Katz, C. A. Ross, and J. A. Johnson, *Emergence of layered nanoscale mesh networks through intrinsic molecular confinement self-assembly*. Nat Nanotechnol **18**, 273-280 (2023). doi:10.1038/s41565-022-01293-z

4 H. Huang, and A. Alexander-Katz. *Dissipative particle dynamics for directed self-assembly of block copolymers.* J Chem Phys **151**, 154905 (2019), doi:10.1063/1.5117839

5 M. Ma, R. Liu, T. Su, Z. Sun, and C. A. Ross, *Reversible Morphology Locking via Metal Infiltration in a Block Copolymer*. ACS Nano **17**, 12225-12233 (2023). doi:10.1021/acsnano.3c00723

6 H. Huang, R. Liu, C. A. Ross, and A. Alexander-Katz, *Self-Directed Self-Assembly of 3D Tailored Block Copolymer Nanostructures.* ACS Nano **14**, 15182-15192 (2020), doi:10.1021/acsnano.0c05417

7 R. Liang, Y. Xue, X. Fu, A. Le, Q. Song, Y. Qiang, Q. Xie, R. Dong, Z. Sun, C. O. Osuji, J. A. Johnson, W. Li, and M. Zhong. *Hierarchically engineered nanostructures from compositionally anisotropic molecular building blocks.* Nat Mater **21**, 1434-1440 (2022). doi:10.1038/s41563-022-01393-0

Center for PRedictive Integrated Structural Materials Science (PRISMS Center)

Lead Investigator: John Allison (Director), johnea@umich.edu
Participating Institutions: University of Michigan and University of California, Santa Barbara
Website: http://prisms-center.org
Keywords: Integrated Multi-Scale Modeling, Magnesium, Microstructural Evolution, Mechanical Behavior

Project Scope

The primary objective of the PRISMS Center is to develop and deploy a unique scientific platform for accelerating predictive materials science. The platform is comprised of advanced open-source software, an information repository and scientific use cases. The suite of four major open-source multi-scale computational tools is designed to predict microstructural evolution and mechanical behavior of metals. The Materials Commons is a sophisticated, user-friendly information repository and collaboration space. The PRISMS Center platform is demonstrated in scientific use cases which accelerate the quantitative and predictive understanding of magnesium alloys.

Relevance to MGI

The PRISMS Center platform of open-source software, Materials Commons and scientific use cases has been designed to form an important and extensible component of the MGI Materials Innovation Infrastructure. Our scientific use cases demonstrate the value of the integration of simulation, experiment, and theory for accelerating predictive understanding important phenomena of metallic materials.

Technical Progress

Over 8000 unique clones have been made of PRISMS Center open-source software (see Fig. 1) with over 1000 downloads over the past year. The codes are updated with new features annually and represent state-of-art computational efficiency and capability. The four major codes are DFT-FE (real space density functional theory), CASM (Cluster Approach to Statistical Mechanics), PRISMS-Plasticity (crystal plasticity finite element) and PRISMS-PF (phase field). Communities of open-source developers are forming around each code. Notable among these open-source developed codes are PRISMS-Fatigue, a code for simulating microstructural effects on fatigue and PRISMS-Indentation, a code for investigating microstructural effects on indentation. Both codes use PRISMS-Plasticity as the simulation engine. Another notable achievement is the Gordon Bell Prize that was awarded to the developers of DFT-FE for its demonstration of high-performance computational capability on the Frontier exascale GPU machine.

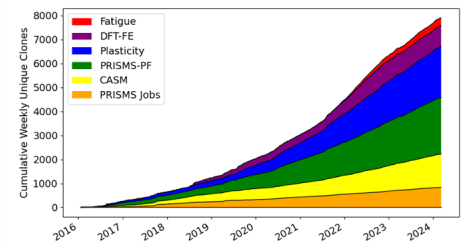


Figure 1. Growing number of cumulative downloads (unique clones) of PRISMS Center open-source software since 2016.

Materials Commons 2.0 is an information repository, a collaboration site and an electronic lab notebook all in one seamless and user-friendly web-based system. It has many features for uploading information, searching, visualizing and using materials information and is frequently updated with new features. There are over 760 registered users of the Materials Commons and it currently securely stores over 6.7M million data files (42TB). Published datasets have been viewed over 28,000 times and downloaded more than 14,000 times.

Our fundamental science is conducted in "scientific use cases" which currently include grain boundary strengthening, alloy effects on twin evolution and alloy effect on texture development and recrystallization. Significant progress has been made in all areas and is documented in over 125 archival papers. In the past year, 18 papers have been published and an additional 6 have been submitted.

Scientific highlights over the past year include:

Grain boundary (GB) strengthening: Using DFT-FE, the largest ab-initio simulation ever conducted to date was used to study the influence of solute (Y) atoms on the <c+a> pyramidal I/II screw dislocation cross-slip barrier in dilute binary Mg-Y alloys (this work was awarded the Gordon Bell Prize). Atomistic simulations were used to

measure the slip transmission energy barriers at pure and solute-segregated Mg grain boundaries. An improvement on Ashby's classic model for grain size dependence of flow stress was developed and calibrated for Mg-Al using nanoindentation testing. This model improvement incorporates both geometrically necessary dislocations and statistically stored dislocations.

Alloy effects on twin evolution: We have applied a systematic framework to quantify the influence of alloying on the formation of twins and detwinning during monotonic and cyclic deformation. This framework involves the use of PRISMS-Plasticity simulations coupled with an array of advanced experimental tools including in-situ high energy diffraction microscopy and in-situ electron back scatter diffraction to quantify twin evolution. We have determined that Al and Zn lead to low resistance to twinning, while Nd, Zn-Ca alloys and Y have increasingly high resistance to twinning. Using a new dark-field high energy x-ray microscopy technique, an important twin nucleation data set has been captured showing twin nucleation at grain boundary triple junctions. PRISMS-Plasticity simulations of this grain neighborhood are underway. Using molecular dynamics simulations, alloy effects on competition between <c+a> slip and twin nucleation have been modeled. A {11-21} twin mechanism, uncommon in Mg alloys, has been discovered experimentally in a Mg-7Y alloy.

Alloy effects on texture evolution and recrystallization: Using PRISMS-Plasticity coupled with thermo-mechanical testing and EBSD characterization of texture, we have demonstrated the ability to predict the influence of Ca, Zn and Ca/Zn in combination on deformation texture. We determined that alloying with >1wt% Zn+Ca reduces the amount of basal slip and twinning while promoting <c+a> slip. This combination produces a weak basal deformation which is key for producing the highly desirable weak annular texture that is subsequently produced by recrystallization during annealing. To simulate the annealing phase, a probabilistic nucleation model has been established and incorporated into the PRISMS-PF recrystallization application. A comprehensive model for predicting grain boundary segregation has been developed and experimentally validated. Alloy effects and segregation effects on grain boundary mobility are being characterized using molecular dynamics simulation. Recrystallization experiments on Mg-Zn-Ca alloys have been completed to parameterize these models.

Future Plans: Detailed future plans have been developed for all PRISMS Software, Materials Commons and the scientific use cases.

Broader Impacts and Workforce Development

PRISMS Center holds an annual workshop to disseminate our scientific results, establish a collaboration network and train users. Over 400 researchers have attended this workshop and been trained in use of one or more PRISMS Tools. In addition, a PRISMS Center You-Tube channel has been established with training for PRISMS software and have been viewed nearly 42,000 times. PRISMS software has also been integrated into graduate courses at UM and Georgia Institute of Technology, as well as short courses at UM and Texas A&M.

Data Management and Open Access

PRISMS Center has four open-source major codes and ancillary codes for use and co-development by the materials community. The Materials Commons information repository functions as a digital laboratory notebook, collaboration platform and public data repository. All data and simulation results from PRISMS Center research are made available to the public via the Materials Commons. Codes and data can be accessed at the following sites:

- DFT-FE: https://github.com/dftfeDevelopers/dftfe
- CASM: https://github.com/prisms-center/CASMcode
- PRISMS-PF: https://github.com/prisms-center/phaseField
- PRISMS-Plasticity: https://github.com/prisms-center/plasticity
- PRISMS-Fatigue: https://github.com/prisms-center/Fatigue
- PRISMS Toolbox: https://github.com/prisms-center/prisms-toolbox
- Materials Commons: https://materialscommons.org

Advancing Along the Materials Development Continuum and Partnerships to Translation

Industrial and national lab researchers have been trained on PRISMS software tools and are using one or more of these codes. The scientific outcomes of our fundamental research projects provide understanding and data (via Materials Commons) that can be used in applied research and development projects as opportunities arise.

Recent Publications (Members of the PRISMS Center have published over 125 papers acknowledging DOE-BES funding. These publications have been cited over 3560 times with a combined impact factor of 37).

1. B Phung, D. Greeley, M. Yaghoobi, J. Adams, J. Allison, A. Spear, "Predicting microstructurally sensitive fatigue-crack path in WE43 magnesium using high-fidelity numerical modeling and three-dimensional experimental characterization", Fatigue and Fracture of Engineering Materials and Structures, 47 (2023) 862. DOI: doi.org/10.1111/ffe.1420.
2. K. Stopka, M. Yaghoobi, J. Allison, D. McDowell, "Microstructure-Sensitive Modeling of Surface Roughness and Notch Effects on Extreme Value Fatigue" International Journal of Fatigue, 166 (2023) 10725. DOI: doi.org/10.1016/j.ijfatigue.2022.107295.
3. A. Lakshmanan, M. Andani, M. Yaghoobi, J. Allison, A. Misra, V. Sundararaghavan, "A combined experimental and crystal plasticity study of grain size effects in magnesium alloys" Journal of Magnesium Alloys 11 (12) (2023) 4445-44.
4. M. Yaghoobi, K. Stopka, D. McDowell, L. Graham-Brady, K. Teferra, "Effect of sample size on the maximum value distribution of fatigue driving forces in metals and alloys" International Journal of Fatigue, 176 (2023) 107853.
5. S. Das, B. Kanungo, V. Subramanian, G. Panigrahi, P. Motamarri, D. Rogers, P. Zimmerman, V. Gavini, "Large-scale materials modeling at quantum accuracy: *Ab initio* simulations of quasicrystals and interacting extended defects in metallic alloys", ACM, SC'23 Denver Co, November 2023. NOTE: 2023 Gordon Bell Prize Winner.
6. J. Kim, Y. Kimura, B. Puchala, T. Yamazaki, U. Becker, W. Sun, "Dissolution enables dolomite crystal growth near ambient conditions", Science, 382 (2023) 915-920.
7. A. Roy, R. Arroyave, V. Sundararaghavan, "Incorporating dynamic recrystallization into a crystal plasticity model for high temperature deformation of Ti-6Al-4V, " Materials Science and Engineering, (2023) 145211.
8. V. Goel, D. Montiel, K. Thornton "Understanding the Effect of Electrochemical Properties and Microstructure on the Microgalvanic Corrosion of Mg Alloys via Phase-Field Simulations", Journal of the Electrochemical Society, 170 (2023), 101502.
9. S. Lee, T. Berman, C. Yildirim, C. Detlefs, J. Allison, A. Bucsek "Multiscale and multimodal characterization of recrystallized and non-recrystallized grains during static recrystallization in a hot-compressed Mg-3.2Zn-0.1Ca wt.% alloy" Scientific Reports, 14,1 (2024) 6241.
10. D. A. Greeley, J. F. Adams, P. Kneissi, J. W. Jones, A. D. Spear, J. E. Allison "Use of Multi-modal HEDM for characterization of fatigue crack paths in Mg WE43", Fatigue and Fracture of Engineering Materials and Structures, 47 (2024) 1150-1171.
11. A. Roy, S. Ganesen, P. Acar, R. Arroyave, V. Sundararaghavan, "Combining crystal plasticity and phase field model for predicting texture evolution and the influence of nuclei clustering on recrystallization path kinetics in Ti-alloys", Acta Materialia, 266 (2024) 119645.
12. S. Das and V. Gavini, "Accelerating self-consistent field iterations in Kohn-Sham density functional theory using a low-rank approximation of the dielectric matrix," Physical Review B, 107 (12) (2024) 125133.
13. A. Tallman, M. Yaghoobi, "PRISMS-Indentation: multi-scale elasto-plastic virtual indentation module", Integrating Materials and Manufacturing (2024) 1-18.
14. V. Menon, S. Das, V. Gavini, L. Qi, "Atomistic simulations and machine learning of solute grain boundary segregation in Mg alloys at finite temperatures", Acta Materialia, 264 (2024) 119515.
15. E. Song, M. Andani, A. Misra, "Investigation of grain size and geometrically necessary dislocation density dependence of flow stress in Mg-4Al by using nanoindentation" Acta Materialia, 265 (2024) 119633.
16. S. Sai Behara, J. C. Thomas, B. Puchala, and A. Van der Ven, "Chemomechanics in alloy phase stability", Phys. Rev. Materials 8, (2024) 033801. DOI: doi.org/10.1103/PhysRevMaterials.8.033801
17. Y. Zhang, M. Yaghoobi, Y. Zhang, D. Rubio-Ejchel, P. Kenesei, J. Park, A. Rollett, J. Gordon, " In situ measurement of three-dimensional intergranular stress localizations and grain yielding under elastoplastic axial-torsional loading" Journal of Materials Research and Technology, 30 (2024) 8792. DOI: doi.org/10.1016/j.jmrt.2024.05.235.
18. E. Song, M. Andani, A. Misra, "Quantification of grain boundary effects on the geometrically necessary dislocation density evolution and strain hardening of polycrystalline Mg-4Al using in situ tensile testing in scanning electron microscope and HR-EBSD" Journal of Magnesium Alloys, 12 (2024) 1815. DOI: doi.org/10.1016/j.jma.2024.05.2021
19. B. Puchala, J. C. Thomas, A. Van der Ven, "CASM Monte Carlo: Calculations of the thermodynamic and kinetic properties of complex multicomponent crystals", in review/edit Computational Materials Science (2024).
20. V. Menon, L. Qi, "Atomistic simulations of competitive nucleation of deformation twinning and pyramidal dislocations from grain boundaries of Mg and Mg alloys", submitted to Computational Materials Science (2024)

AI-Guided Accelerated Discovery of Multi-Principal Element Multi-Functional Alloys

Lead Investigator: Raymundo Arroyave, rarroyave@tamu.edu
Participating Institutions: Texas A&M Engineering Experiment Station
Source of Support: NSF-DMREF-2119103
Website: none
Keywords: Multi-functional alloys, Shape Memory Alloys, Machine learning, Bayesian optimization

Project Scope

Discovering multi-principal element multi-functional alloys (MPEMFAs) with extreme property combinations, such as ultra-high temperature martensitic transformations (MT) with low hysteresis, stable reversible shape change under stress, superelasticity at temperatures significantly beyond state-of-the-art; extreme properties, such as Invar and Elinvar effects up to 700◦C; or uniquely tailored properties, such as SMAs-as-phase-change-materials (PCMs) with high thermal conductivity and transformation enthalpy but also with widely different MT temperatures, enabling adaptive thermal energy storage/conversion/management systems in a wide temperature range.

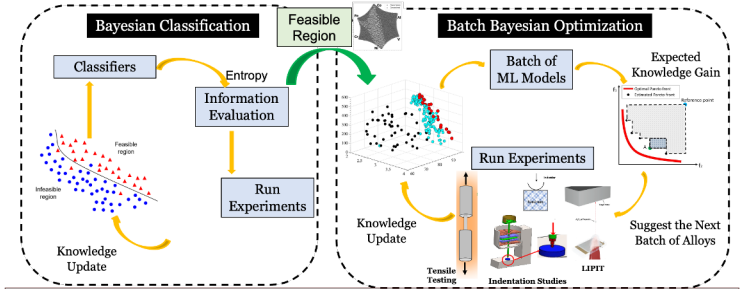


Figure 1. Constrained Multi-Information Source Batch Bayesian Optimization.

Relevance to MGI

Once a materials problem has been defined, a major challenge is how to efficiently explore and exploit the materials design space. Unfortunately, current alloy development frameworks fall far short of this challenge. Methods based on traditional Integrated Computational Materials Engineering (ICME) for example, (i) build and exploit process-structure-property-performance (PSPP) relationships at a considerable computational expense; (ii) do not readily incorporate data from experiments within their framework; and (iii) are sequential, which means that they tend to be deployed by evaluating materials design choices one-at-a-time. *Traditional high-throughput (HTP) combinatorial* computational and experimental approaches, on the other hand, are (i) incapable of dealing with the high dimensionality and complexity of the materials space; and (ii) are 'one-shot' or 'open loop' schemes without a built-in iterative framework, and are unable to prescribe future actions given the current state of knowledge. *Moreover, traditional ICME and HTP approaches are suboptimal in resource utilization.*

To address these issues, we have developed a Constrained Multi Information Source Batch Bayesian Optimization (CMISSBO) framework that **incorporates the strengths of ICME and combinatorial methods while addressing all their weaknesses,** as it: (i) combines advanced simulations, physics-based and ML models with phase stability analysis, and advanced alloy search schemes to efficiently identify the feasible regions amenable to optimization; (ii) exploits correlations *to fuse simulations and experiments* to obtain efficient ML models for predicting PSPP relations; (iii) uses Bayesian Optimization (BO) to make globally optimal iterative decisions on where to explore/exploit the materials space, leveraging existing models and data; (iv) leverages the team's newly developed batch modifications to BO (Batch BO) that enable the iterative and optimal exploration/exploitation of the design space *evaluating multiple solutions at once*; and (v) is capable of accounting for multiple objectives and constraints *simultaneously*.

Our framework is directly relevant to the MGI as it seamlessly integrates experiments and simulations, takes advantage of novel AI/ML tools, incorporates modern approaches to high-throughout alloy discovery, and carries out the discovery in iterative loops in which each iteration provides improved knowledge over the materials space being explored.

Technical Progress

We have already employed this framework to discover a NiTiCuHf alloy with the lowest recorded thermal hysteresis with transformation temperatures between 250℃ and 350℃ to date without the need to incorporate expensive precious metals. Notably, our optimization scheme was able to prescribe not only chemistry but also processing conditions.

In addition to this discovery, numerous contributions have been made on the methodology front:

Bayesian Optimization and Modeling: Advances in Bayesian optimization and modeling techniques have significantly enhanced the efficiency and accuracy of materials design. These methods enable multi-objective optimization, uncertainty quantification, and adaptive experimental design, leading to improved prediction of material properties and accelerated discovery processes.

Predictive Modeling: The development of predictive models and machine learning frameworks has enabled more accurate and interpretable predictions of material properties. Techniques such as deep learning, graph networks, and boosting-based models are being used to predict transformation temperatures, phase constitution, and crystal properties with high precision.

High-Throughput and Data-Driven Approaches: High-throughput and data-driven methodologies are revolutionizing materials discovery by enabling rapid exploration and analysis of vast material spaces. These approaches leverage large datasets and advanced computational techniques to uncover novel materials and optimize their properties efficiently. Through this project, we have developed extensive datasets that can be used for further method improvement and method validation.

Future Plans

We plan to cover the missing pieces of the current efforts in connecting scientific approaches to explore the design space, perform targeted design steps using optimization tools, and evaluate the discoveries using experimental approaches. The ultimate goal is discovering MPEMFA, not only for a specific element group but in a much more diverse design space in terms of the elements and the number of elements included in each material.

Broader Impacts and Workforce Development

The team is actively involved in nurturing the next generation of experts through the Texas A&M Computational Materials Science Summer School, now in its thirteenth successful year. Organized by Principal Investigator Raymundo Arroyave, this prestigious program delivers an intensive, 10-day training experience covering state-of-the-art computational materials science methods. The curriculum spans multiple scales and incorporates cutting-edge topics such as machine learning, artificial intelligence, and materials design. Participants gain hands-on exposure to various simulation techniques and predictive tools essential for advancing material behavior understanding.

Data Management and Open Access

Following FAIR data practices, all the research's datasets and source codes are published on GitHub. The following repositories belong to the published articles:

- https://github.com/sinazadeh/CatBoost-SMAs
- https://github.com/sinazadeh/Phase-Compatibility-Model-NiTi

Advancing Along the Materials Development Continuum and Partnerships to Translation

Our study achieved a significant milestone by identifying the narrowest hysteresis observed to date in the quaternary HT-SMA temperature space, and notably, without incorporating precious materials. This breakthrough was facilitated by leveraging extensive datasets from both literature and our own experiments, coupled with advanced machine-learning models and optimization platforms. These tools enabled rapid exploration within the expansive compositional space, enhancing the efficiency and effectiveness of our research.

Publications and References

1. Zadeh, S.H., Behbahanian, A., Broucek, J., Fan, M., Vazquez, G., Noroozi, M., Trehern, W., Qian, X., Karaman, I. and Arroyave, R. *An Interpretable Boosting-Based Predictive Model For Transformation Temperatures Of Shape Memory Alloys*. Computational Materials Science, **226**, p.112225 (2203). DOI: 10.1016/j.commatsci.2023.112225
2. Arróyave, R., Khatamsaz, D., Vela, B., Couperthwaite, R., Molkeri, A., Singh, P., Johnson, D.D., Qian, X., Srivastava, A. and Allaire, D. *A Perspective On Bayesian Methods Applied To Materials Discovery And Design*. MRS Communications, **12**(6), pp.1037-1049 (2022). DOI: 0.1557/s43579-022-00288-0
3. Khatamsaz, D., Vela, B. and Arróyave, R., 2023. *Multi-Objective Bayesian Alloy Design Using Multi-Task Gaussian Processes*. Materials Letters, **351**, p.135067 (2023). DOI: 10.1016/j.matlet.2023.135067
4. Lei, B., Kirk, T.Q., Bhattacharya, A., Pati, D., Qian, X., Arroyave, R. and Mallick, B.K.. *Bayesian Optimization With Adaptive Surrogate Models For Automated Experimental Design*. Npj Computational Materials, **7**(1), p.194. (2021). DOI: 10.1038/s41524-021-00662-x
5. Zadeh, S.H., Cakirhan, C., Khatamsaz, D., Broucek, J., Brown, T.D., Qian, X., Karaman, I. and Arroyave, R. *Data-Driven Study Of Composition-Dependent Phase Compatibility In Niti Shape Memory Alloys*. *arXiv preprint arXiv:2402.12520*. (2024). DOI: 10.48550/arXiv.2402.12520
6. Yu, H., Liu, M., Luo, Y., Strasser, A., Qian, X., Qian, X. and Ji, S. *Qh9: A Quantum Hamiltonian Prediction Benchmark For Qm9 Molecules*. Advances in Neural Information Processing Systems, **36**. (2024). DOI:
7. Roy, A.M., Bose, R., Sundararaghavan, V. and Arróyave, R. *Deep Learning-Accelerated Computational Framework Based On Physics Informed Neural Network For The Solution Of Linear Elasticity*. Neural Networks, **162**, pp.472-489 (2023). DOI:10.1016/j.neunet.2023.03.014
8. Vela, B., Acemi, C., Singh, P., Kirk, T., Trehern, W., Norris, E., Johnson, D.D., Karaman, I. and Arróyave, R. *High-Throughput Exploration Of The Wmovtanbal Refractory Multi-Principal-Element Alloys Under Multiple-Property Constraints*. Acta Materialia, **248**, p.118784 (2023). DOI:10.1016/j.actamat.2023.118784
9. Khatamsaz, D., Vela, B., Singh, P., Johnson, D.D., Allaire, D. and Arróyave, R. *Multi-Objective Materials Bayesian Optimization With Active Learning Of Design Constraints: Design Of Ductile Refractory Multi-Principal-Element Alloys*. *Acta Materialia*, **236**, p.118133. (2022). DOI:1016/j.actamat.2022.118133
10. Khatamsaz, D., Neuberger, R., Roy, A.M., Zadeh, S.H., Otis, R. and Arróyave, R. *A Physics Informed Bayesian Optimization Approach For Material Design: Application To Niti Shape Memory Alloys*. npj Computational Materials, **9**(1), p.221. (2023) DOI: 10.1038/s41524-023-01173-7
11. Zhao, G., Dougherty, E., Yoon, B.J., Alexander, F. and Qian, X. *Efficient Active Learning For Gaussian Process Classification By Error Reduction*. Advances in Neural Information Processing Systems, *34*, pp.9734-9746 (2021).
12. Vazquez, G., Chakravarty, S., Gurrola, R. and Arróyave, R. A *Deep Neural Network Regressor For Phase Constitution Estimation In The High Entropy Alloy System Al-Co-Cr-Fe-Mn-Nb-Ni*. npj Computational Materials, **9**(1), p.68. (2023). DOI: 10.1038/s41524-023-01021-8
13. Yan, K., Fu, C., Qian, X., Qian, X. and Ji, S. *Complete And Efficient Graph Transformers For Crystal Material Property Prediction*. arXiv preprint arXiv:2403.11857 (2024) DOI:10.48550/arXiv.2403.11857
14. Qian, X., Yoon, B.J., Arróyave, R., Qian, X. and Dougherty, E.R. *Knowledge-Driven Learning, Optimization, And Experimental Design Under Uncertainty For Materials Discovery*. Patterns, **4**(11) (2023).
15. Arróyave, R. *Phase Stability Through Machine Learning*. Journal of Phase Equilibria and Diffusion, **43**(6), pp.606-628. (2022). DOI: 10.1007/s11669-022-01009-9
16. Singh, P., Vela, B., Ouyang, G., Argibay, N., Cui, J., Arroyave, R. and Johnson, D.D. *A Ductility Metric For Refractory-Based Multi-Principal-Element Alloys*. *Acta Materialia*, **257**, p.119104 (2023). DOI:10.1016/j.actamat.2023.119104
17. Trehern, W., Hite, N., Ortiz-Ayala, R., Atli, K.C., Sharar, D.J., Wilson, A.A., Seede, R., Leff, A.C. and Karaman, I., *NiTiCu Shape Memory Alloys With Ultra-Low Phase Transformation Range As Solid-State Phase Change Materials*. Acta Materialia, **260**, p.119310 (2023). DOI:1016/j.actamat.2023.119310
18. Vela, B., Khatamsaz, D., Acemi, C., Karaman, I. and Arróyave, R. *Data-Augmented Modeling For Yield Strength Of Refractory High Entropy Alloys: A Bayesian Approach*. Acta Materialia, **261**, p.119351 (2023). DOI: 10.1016/j.actamat.2023.119351
19. Khatamsaz, D., Arroyave, R. and Allaire, D.L., 2024. Asynchronous Multi-Information Source Bayesian Optimization. Journal of Mechanical Design, **146**(10). DOI: 10.1115/1.4065064
20. Trehern, W., Ortiz-Ayala, R., Atli, K.C., Arroyave, R. and Karaman, I. *Data-driven shape memory alloy discovery using artificial intelligence materials selection (AIMS) framework*. Acta Materialia, **228**, p.117751 (2022). DOI: 10.1016/j.actamat.2022.117751

Optimizing Problem formulaTion for prIntable refractory alloys via integrated MAterials and processing co-design (OPTIMA)

Lead Investigator: Raymundo Arróyave, e-mail: *raymundo.arroyave@tamu.edu*
Participating Institutions: Texas A&M University
Source of Support: NSF-DMREF-2323611.
Website: N/A
Keywords: Bayesian Optimization, Problem Optimization, Human-in-the-loop, Printable Refractory Alloy, Additive Manufacturing

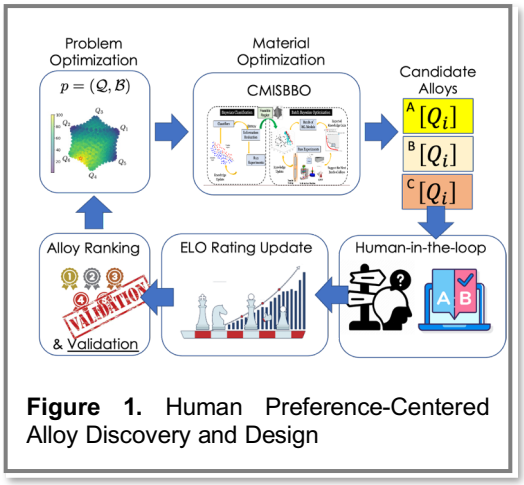


Figure 1. Human Preference-Centered Alloy Discovery and Design

Project Scope

This project aims to develop a dynamic problem formulation and optimization framework to enhance the discovery of printable refractory alloys (PRAs). Specifically, the project targets PRAs for high-temperature transportation, power generation, and national security applications. The research involves integrating physics-based models, machine learning, and high-throughput experiments to optimize alloy performance and manufacturability while considering supply chain risks. Key innovations include a Problem Optimization Space Bayesian Optimization (POSBO) approach based on human-in-the-loop feedback for dynamic problem adjustments **(Fig 1)**. Identifying and validating alloys meeting performance, manufacturability, and supply chain criteria will measure success.

Relevance to MGI

The project aligns closely with the Materials Genome Initiative (MGI) goals, as outlined in the 2021 MGI strategic plan. It integrates experimental, computational, and theoretical efforts through a closed, iterative feedback loop, harnessing the power of data to accelerate materials discovery. This integration is achieved via the Problem Optimization Space Bayesian Optimization (POSBO) framework, which dynamically adjusts problem formulations based on real-time decision-maker input and evolving constraints. The collaborative process involves synergistic interactions between Synthesis, characterization, and modeling efforts. Synthesis and processing activities produce candidate printable refractory alloys (PRAs), which are characterized using high-throughput techniques to measure properties. The resulting data is fed into computational models to refine predictions and guide subsequent experimental iterations.

Technical Progress

We developed a novel computational framework to explore multicomponent systems for efficient search inside multiple objectives' entire chemistry design space. This framework makes our complex search space a polar and cylindrical coordinate space for odd and even numbers of component systems, respectively **(Fig 2)**. Using this framework, we implemented a Multi-Objective Bayesian Optimization (MOBO) integrated with CALPHAD simulations to efficiently navigate the multi-principal component design space (a quinary system) by addressing the critical trade-offs between optimizing conflicting objectives, e.g., crack susceptibility and yield strength—factors that significantly influence the performance and manufacturability in Additive Manufacturing processes **(Fig 3)**. This multi-objective optimization gives a solution for the alloy design (as defined by the Pareto set); our innovative framework at this stage calls the human inside the loop to guide selecting the best alloy for specific design tasks by optimizing the problem formulation space.

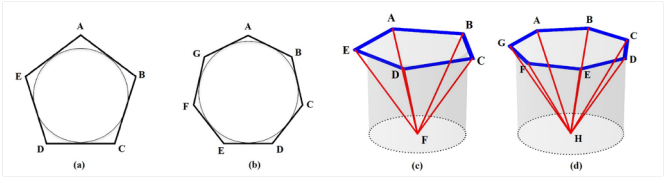


Figure 2. (a), (b) framework for screening inside odd number of component system (reduced to a polar coordinate), quinary and septenary system, respectively; (c), (d) for even number of component system (reduced to a cylindrical coordinate), senary and octonary system, respectively.

Synopsis of the Proposed Work

In tandem with material optimization **(Fig 3a)** (multi-objective optimization in the chemistry space), our innovative framework optimizes the problem definition itself **(Fig 3b)** because, in materials discovery, a design (problem solution) may be a poor fit to a discovery task but may be an excellent fit for another task. So, for different materials design tasks, even if the multiple objectives are the same, the weights of these quantities of interest need to be optimized for different tasks, necessitating the human in the optimization loop to rate the candidate alloys at the Pareto frontier hypersurface of a multi-objective optimization problem. So, the key innovations are (a) the inclusion of problem formulation within the design optimization loop and (b) the rigorous incorporation of decision-maker preferences within the discovery/design loop. The framework rigorously incorporates decision-maker preferences within the discovery loop by utilizing an Elo-based rating system to compare pairs of candidate solutions and adjust preferences based on new information **(Fig 1)**. After identifying the candidate chemistries, vacuum arc melting (VAR) will synthesize large samples. A *Rapid Alloy Prototyper* (RAP) will also be employed, based on a laser direct energy deposition (DED)-based additive manufacturing Synthesis involves vacuum arc melting (VAR) and a Rapid Alloy Prototyper (RAP) to fabricate and optimize alloy samples. Characterization techniques like SEM, EDS, XRD, and EPMA will ensure precise analysis of microstructure and properties. This dynamic, human-in-the-loop framework aims to accelerate materials discovery by allowing real-time adaptation to changing constraints and objectives, including externalities like supply chain risks, ultimately enhancing the performance and applicability of the materials solutions.

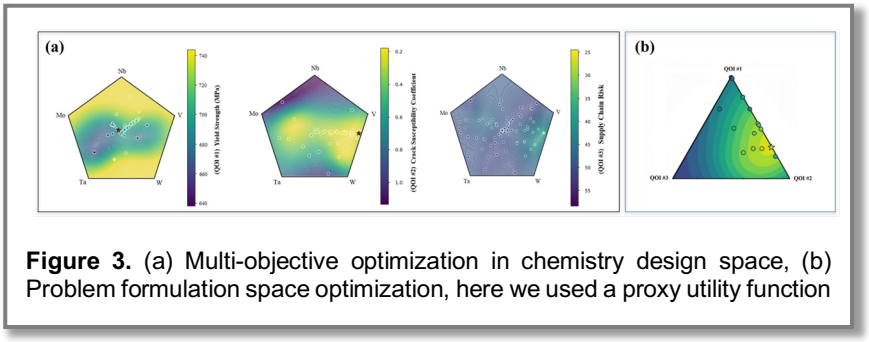


Figure 3. (a) Multi-objective optimization in chemistry design space, (b) Problem formulation space optimization, here we used a proxy utility function

Broader Impacts and Workforce Development

The research team leverages the Data-Enabled Discovery and Development of Energy Materials (D3EM) program at Texas A&M University, supported by the NSF NRT program, to provide interdisciplinary training in materials science, informatics, and design. Students involved in this project are gaining hands-on experience with the novel co-design framework and tackling real-world materials discovery problems using machine learning and AI-based frameworks through the Materials Design Studio (MDS) course. At least 25 students enrolled in the Materials Design Studio (MDS) course in Spring 2024. Besides the theory classes, outstanding lab sessions were provided on hands-on Materials discovery using Bayesian Optimization. From the innovative works carried out in this course, six final projects are completed, which are expected to be published as peer-reviewed papers. Collaborations with industry partners and government laboratories, such as the Army Research Laboratory and NASA Glenn Research Center, will facilitate translating research outcomes into practical applications.

Data Management and Open Access

The project's data management ensures that all digital outputs will be readily accessible and valuable to the broader materials research community. Data from experiments and computations are combined into a comprehensive, searchable materials data infrastructure organized within the framework of process-structure-property relationships. This structure is maintained through a hierarchical and logical file system, ensuring data traceability and accessibility. Following the same approach of disseminating a synthetic microstructure dataset (the open phase field microstructure database), we plan to share our simulation augmented AM database as the *Additive Manufacturing Atlas*.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The project will produce open-source software and maintain open-access databases, promoting the disseminating of knowledge and tools developed. Additionally, the commercialization of designed alloys will be pursued through collaborations with industry partners, leveraging the PIs' extensive experience in commercializing research outputs through start-up companies.

Publications and References

(Supported by this award)

1. Sheikh, S., Vela, B., Attari, V., Huang, X., Morcos, P., Hanagan, J., Acemi, C., Karaman, I., Elwany, A. and Arroyave´, R., 2024. *Exploring Chemistry and Additive Manufacturing Design Spaces: a Perspective on Computationally-guided Design of Printable Alloys*. Materials Research Letters, 12(4), pp.235-263. DOI:10.1080/21663831.2024.2316204
2. Morcos, P., Vela, B., Acemi, C., Elwany, A., Karaman, I., and Arroyave, R., *Data-Augmented Modeling for Melt Pool Dimensions in Laser Powder Bed Fusion: A Bayesian Approach*. Available at SSRN 4814164

DMREF: Organic Materials Architectured for Researching Vibronic Excitations with Light in the Infrared (MARVEL-IR)

Lead Investigator: Jason D. Azoulay, jdazoulay@gatech.edu
Participating Institutions: Georgia Institute of Technology (**J. D. Azoulay**, **G. Hu**), City University of New York (**M. Y. Sfeir**), University of California San Diego (**T. N. Ng**), University of California Riverside (**B. M. Wong**), Air Force Research Labs (AFRL, **J. Vella**), Brilliant Matters (**P. Berrouard**).
Source of Support: NSF-DMREF, AFRL, AFOSR.
Website: none
Keywords: AFRL, Conjugated Polymers, Optoelectronics, Semiconductor, Computational Chemistry

Project Scope

Infrared (IR) photodetectors underpin modern science, technology, and society in profound ways. However, current IR semiconductors possess numerous drawbacks that limit their widespread use and the development of emerging technologies. To overcome this limitation, the **MARVEL–IR** project will revolutionize our understanding of charge photogeneration and emerging solid-state transport phenomena to develop a new generation of conjugated polymers that enable optical to electrical transduction of IR light. Our complete interdisciplinary program combines quantum dynamics calculations, beyond DFT approaches, high-throughput computation, and an integrated feedback loop with synthesis, spectroscopy, and device fabrication to enable a *new fundamental capability for organic materials that will serve as a core enabler of transformative technologies.*

Relevance to MGI

Our DMREF team is developing *the first* examples of design guidelines for conjugated polymers (CPs) that show a photoresponse spanning the short-, mid-, long-wave IR (SWIR-LWIR, λ = 1–14 μm); a primary window for modern scientific, industrial, energy, medical, space, defense, quantum, and numerous other applications. To achieve this, **MARVEL–IR** is addressing grand challenges in a program that forms a closed loop between theory, synthesis, spectroscopy, device fabrication, and computation. Revolutionary *ab initio* and time-dependent quantum chemical calculations that incorporate non-adiabatic dynamics are *for the first-time* providing detailed insight into IR excitations in correlated organic materials with complex excitonic, vibrational, polaronic, and spin properties. Systematic theory-synthesis-spectroscopic approaches are being developed and applied to benchmark these new theoretical approaches and correlate molecular design with emerging functionality and coherent quasiparticle dynamics across multiple spatiotemporal timescales. This is being related to the fundamental electro-optical physics and device performance. New, foundational design principles will eventually be combined with experimentally validated physical structure-property models and data-driven machine learning methods to simulate new polymer structures, rapidly screen materials candidates, improve performance, and create a comprehensive materials genome for CPs that operate throughout the IR.

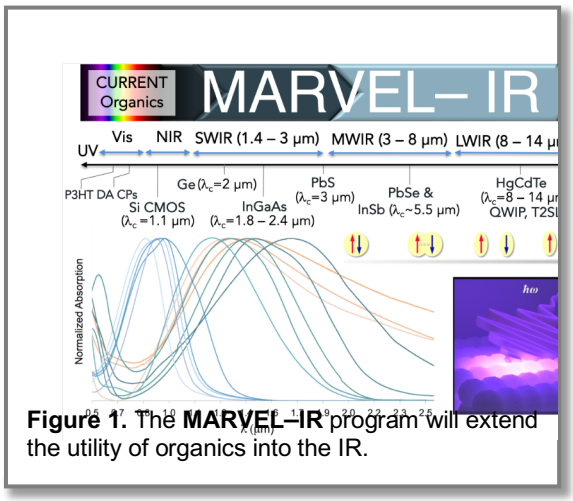
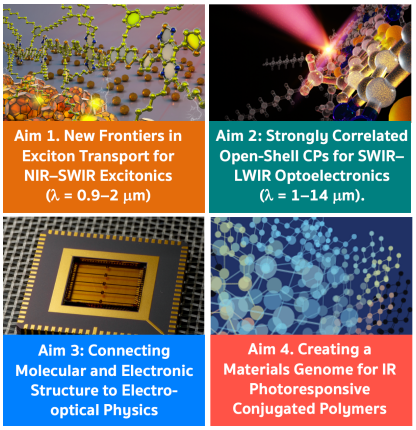


Figure 1. The **MARVEL–IR** program will extend the utility of organics into the IR.

Technical Progress

Four research aims holistically span fundamental advances in theory, synthesis, spectroscopy, device physics, and computation. Our team is: (1) pioneering the use of advanced computational approaches (density functional tight binding (DFTB) for large/disordered systems and real-time, time-dependent DFT (RT-TDDFT)) to provide *the first* understanding of non-adiabatic dynamics in narrow bandgap CPs; (2) understanding the role of structural and electronic properties on long-range quasiparticle transport (**Aim 1**); (3) relating excited state properties to

molecular design in correlated open-shell CPs through systematic theory-synthesis-spectroscopic approaches (**Aim 2**); (4) developing, applying, and automating advanced tools that allow for temporal resolution of IR excitations and coherent quasiparticle dynamics across multiple spatiotemporal timescales (**Aim 1 & 2**); and (5) creating foundational knowledge to connect molecular and electronic structure to electro-optical physics and performance (**Aim 3**).



In combination with these fundamental efforts, we demonstrated a new approach to suppresses noise in organic photodiodes (OPDs) by diluting the transport and trapping sites using an insulative polymer within the blend. The resulting detectivity (D^*, the figure of merit for detector signal-to-noise ratio) from 600–1400 nm under an applied bias of −2 V was improved by two orders of magnitude, from 10^8 to 10^{10} Jones (cm $Hz^{1/2}$ W^{-1}). This broadly applicable strategy reduces noise in IR-OPDs enabling their *practical operation* and the realization of emerging technologies (*Adv. Funct. Mater.* **2024**, 2314210). Our team has also been studying the response of photoconductive detectors to blackbody radiation at low photon fluxes, which mirrors incident power levels emanating from real-world objects. This is necessary to enable practical application and technology translation. Recent efforts spanning the synthesis of new open-shell CP materials have resulted in $D^* > 10^{10}$ Jones in the IR at room temperature, greatly exceeding state-of-the-art. This performance is competitive with commercial blackbody-sensitive technologies and exceeds other classes of emerging semiconductor materials.

Future Plans

In **Aim 1**, we will continue to understand emergent quasiparticle properties through developing advanced computational methods. Innovations in synthesis will produce CPs with the requisite energetic order and long-range electronic couplings to support the study of emergent transport phenomena, benchmark theory, and articulate structure-property-function relationships in the IR. We will develop spectroscopic methods for correlating vibrational, coherent, and IR excited state characteristics within these emerging semiconductors. In **Aim 2**, we will understand what *ab initio* methods can define excitations in open-shell CPs with complex excitonic, polaronic, and spin behavior. We will combine/extend state-of-the-art DFTB and RT-TDDFT approaches, systematic synthesis, magnetic characterization, ultrafast and THZ spectroscopy, and quantum dynamical modeling to understanding the underlying physical and chemical principles of function. In **Aim 3**, we will understand how molecular features impact the basic electro-optical physics, device performance, noise, and understand the ultimate limits of functionality. These new, foundational design principles will be combined with experimentally validated physical structure-property models and data-driven machine learning methods in **Aim 4**.

Broader Impacts and Workforce Development

Workforce development efforts are focusing on the pillars of multidisciplinary education through co-mentorship, industry and DoD interactions, outreach to underrepresented students, and professional development actives for research and leadership training. The Center for Organic Photonics and Electronics (Azoulay is director) organized two workshops and hosted renowned scientists with emerging IR optoelectronic technologies as a core theme. This enabled team and community building, thought leadership, reputation enhancement, and to act as an effective focal point for interactions with external partners. Efforts related to the development of IR sensors are ongoing between GT and AFRL. The program is strengthening AFRL-academia interactions by (1) further capitalizing on current disruptive technology innovations; (2) increasing TRL; (3) promoting technology development and transfer; and (4) better integrating academic researchers to collaborate with AFRL.

Data Management and Open Access

All computational data has been stored in backup hard drives and within computing centers. Data/codes have been stored and disseminated to GitHub, which allows them to be findable and accessible.

Advancing Along the Materials Development Continuum and Partnerships to Translation

All branches of the military face the same challenges associated with EO/IR technologies and our research is being disseminated to others within DoD. We are working with an established company in the field of organic electronics to scale our materials for direct insertion into current manufacturing processes and inclusion within the value chain of both small and medium-sized enterprises (SMEs) and larger companies.

Publications and References

1. T. Bills, C.-T. Liu, J. Lim, N. Eedugurala, P. Mahalingavelar, B. Seo, E. T. Hanna, T. N. Ng, J. D. Azoulay, *A General Strategy for Enhancing Sensitivity and Suppressing Noise in Infrared Organic Photodetectors Using Non-Conjugated Polymer Additives*, *Adv. Funct. Mater*., 2314210 (2024). DOI: 10.1002/adfm.202314210

2. B. Seo, J. Chung, N. Eedugurala, J. D Azoulay, H. J. Kim, T. N. Ng, *Bias Dependence of Organic-Oxide Phototransistors with Peak Infrared Absorption at 1550 nm, ACS Appl. Electron. Mater.*, **5**, 6401–6407 (2024). DOI: 10.1002/adfm.202314210

3. J. D Azoulay, *Infrared Photodetection Using Narrow Bandgap Conjugated Polymers, Proc. SPIE PC12883, Organic Photonic Materials and Devices XXVI,* PC128830A (2024). DOI: 10.1117/12.3000525

Chemical Catalysis for Bioenergy Consortium Data Hub Development

Lead Investigator: Frederick Baddour, Frederick.Baddour@nrel.gov
Participating Institutions: National Renewable Energy Laboratory
Source of Support: DOE-EERE BETO.
Website: https://chemcatbio.org ; https://cpd.chemcatbio.org ; https://catcost.chemcatbio.org

Keywords: Bioenergy, Catalysis, Workflow Acceleration, Open-source, Cost Estimation

Project Scope

The Chemical Catalysis for Bioenergy Consortium (ChemCatBio) Data Hub project accelerates the catalyst and process development cycle by providing (1) a secure repository and plug-ins for centralized data storage and sharing and (2) advanced analytics tools to provide predictive capabilities for catalyst research and development. The vision of this project is the development of a *Catalyst Design Engine* (CDE), a pathway-independent tool that evaluates the trade-off between predicted performance and material cost of catalysts for producing a diversity of end-products from biomass and waste resources.

Relevance to MGI

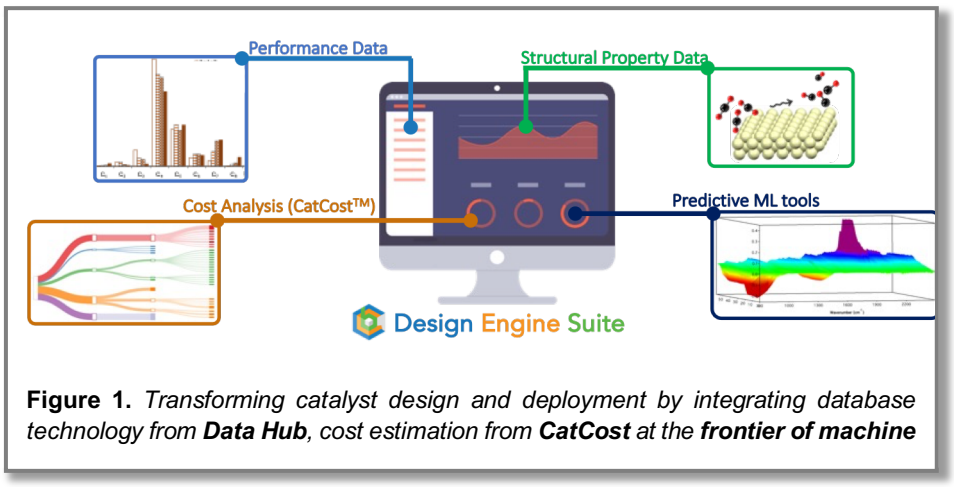


Figure 1. *Transforming catalyst design and deployment by integrating database technology from **Data Hub**, cost estimation from **CatCost** at the **frontier of machine***

The Catalyst Design Engine (CDE) concept is to use rapid, data-driven hypotheses to accelerate experimental advancement of catalysis to hasten the deployment of biomass conversion technologies. The goals include (1) reducing redundancy in catalysis research by providing data in a central, searchable location (i.e., the Catalyst Property Database, https://cpd.chemcatbio.org), (2) enabling computational catalyst screening for complex biomass conversion applications through development of tools and incorporation into AI/ML workflows for descriptor discovery, and (3) incorporating economics into predictive catalyst design through incorporation of the CatCost™ tool. The Catalyst Design Engine is an ambitious vision to accelerate catalyst discovery, offering powerful insight to complement and inform traditional catalyst material design. This concept is central to the ChemCatBio vision of decarbonizing of the domestic economy by accelerating the catalyst development and deployment cycle by coupling advanced enabling capabilities (e.g., catalyst synthesis, characterization, and analysis) with emerging fuel production pathways from biomass derived feedstocks.

Technical Progress

Initial efforts in this project focused on developing a secure data repository for storage and sharing of data amongst project team members that was released publicly in 2018. With the data repository in place, the focus of the ChemCatBio Data Hub project shifted towards the development of transformational tools to enable predictive capabilities in catalyst R&D. In 2020 the Catalyst Property Database (CPD), a Computational Catalyst Database web application, was publicly released. This database consists of curated, previously-computed catalyst property

data mined from the published scientific literature alongside sophisticated search and filtering functions as well as basic data visualization that address the computational catalyst property data needs of catalysis researchers. Realizing the CDE vision requires that developed building blocks (Figure 1), namely CatCost and the Catalyst Property Database, are powerful, expert-vetted tools with substantial buy-in from the catalyst and process development community. Keeping the building blocks relevant and active is critical to ensuring that the overarching CDE offers accurate and up-to-date insight. Toward this goal, this project developed user resources including extensive documentation, opened the database to community uploads, and upgraded the UI to reflect user feedback. Additional novel datasets were generated and released focusing on contaminants relevant to catalyst deactivation, as well as a reference species interconversion (RSI) feature that differentiates this resource from other computational databases.

Future Plans

Future efforts within this project will focus on filling data gaps and developing an integration strategy for the developed tools and databases into an AI/ML workflow for accelerating catalyst discovery. The recently expanded database that includes experimental catalysis datasets and catalyst physical properties will be leveraged in this effort and enable the realization of the FY25 goals of demonstrating an integrated application of the Catalyst Design Engine vision. This will involve using targeted AI/ML methods with at least two distinct Catalyst Property Database data sets (e.g., theoretical adsorption energies, experimental conversion/selectivity) to make predictions within a Catalyst Design Engine paradigm to help experimentalist address current challenges (e.g., mitigate deactivation, reduce process cost).

Broader Impacts and Workforce Development

A critical element associated with the development of advanced scientific databases and analysis tools is overcoming barriers to adoption of these systems in the workflow of scientists across the catalysis community. Towards this end, considerable effort has been focused on the development of educational resources including live and pre-recorded webinars and tutorials as well as workshops at technical conferences. These resources are available at the ChemCatBio website (https://chemcatbio.org) Coupled with these efforts are user engagement and feedback seeking exercises to maintain proper alignment with current and potential use cases and reduce UX barriers for users across sectors (i.e., academia, industry, government).

Data Management and Open Access

Core to the development of the Energy Material Network Data Hubs is the belief that sound data management practice is critical to scientific discovery. This Data Hub project follows the FAIR guiding principles wherever possible and supports users in doing the same by hosting non-proprietary, unencrypted, uncompressed and largely human-readable data. In addition, this project provides support to users in the form of resources for applying data management practices, including documentation of metadata, user tutorials and workflow documentation, which are all available within the public domain.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The overarching objective of this project is to enable the ChemCatBio consortium and the bioenergy industry to accelerate the catalyst and process development cycle through development of publicly available advanced analytics tools and databases. Specifically, this project seeks to achieve this by (1) reducing redundancy (computational cost) in catalysis research by providing data in a central, searchable location, (2) enabling computational catalyst screening for complex biomass conversion applications through development of tools for incorporation with AI/ML workflows for descriptor discovery, and (3) incorporating economics into predictive catalyst design through incorporation of the CatCost™ tool.

Publications and References

1. M. A. Nolen, S. A. Tacey, M. A. Arellano-Treviño, K. M. Van Allsburg, and C. A. Farberow. *High-throughput dataset of impurity adsorption on common catalysts in biomass upgrading applications*, *Materials Cloud Archive* **2024.64** (2024). DOI: https://doi.org/10.24435/materialscloud:4w-70

2. B. E. Petel, K. M. Van Allsburg, and F. G. Baddour, *Cost-Responsive Optimization of Nickel Nanoparticle Synthesis* Advanced Sustainable Systems 2300030 (2023**).** DOI: https://doi.org/10.1002/adsu.202300030

3. L. R. Karadaghi, B. Pan, F. G. Baddour, N. Malmstadt, and R. L. Brutchey *A techno-economic approach to guide the selection of flow recyclable ionic liquids for nanoparticle synthesis*, RSC Sustain. **1**, 1861-1873**.** (2023). DOI: https://doi.org/10.1039/D3SU00182B

4. K. M. Van Allsburg, E. C.D. Tan, J. D. Super, J. A. Schaidle, and F. G. Baddour, *Early-stage evaluation of catalyst manufacturing cost and environmental impact using CatCost*, Nat. Catal. **5**, 342 (2022). DOI: https://doi.org/10.1038/s41929-022-00759-6

5. R. R. White, K. Munch, N. Wunder, N. Guba, C. Sivaraman, K. M. Van Allsburg, H. Dinh, and C. Pailing, *Energy Material Network Data Hubs,* Int. J. Adv. Comp. Sci. & App. **12,** 657. **(**2021) DOI: https://doi.org/10.14569/IJACSA.2021.0120677

6. F. G. Baddour, L. Snowden-Swan, J. D. Super, K. M. Van Allsburg, *Estimating Precommercial Heterogeneous Catalyst Price: A Simple Step-Based Method* Org. Process Res. Dev. **22**, 1599 (2018). DOI: https://doi.org/10.1021/acs.oprd.8b00245

Physics-informed meta-learning for design of complex materials

Lead Investigator: Stephen Baek, baek@virginia.edu
Participating Institutions: University of Virginia, University of Iowa
Source of Support: NSF-DMREF
Website: https://tinyurl.com/materiq
Keywords: Physics-informed machine learning, meta-learning, multi-scale, AI, materials by design.

Project Scope

This multidisciplinary project harnesses recent innovations in artificial intelligence (AI) to establish a novel design and discovery cycle for complex materials that will dramatically accelerate material innovations. A wide class of materials has complex microstructures, which play a dominant role in determining their properties. We are creating new methodologies through which human scientists and AI will collaborate to discover optimal microstructural designs of such materials for targeted properties and performance. A particular focus will be on energetic materials (EM), which are the archetype of materials with strong microstructure influence.

Relevance to MGI

Our long-term vision is to achieve disruptive innovation for material discovery, through convergence of computational design and AI. The scientific premise is that microstructure and geometry at meso-scale—as much as chemistry at a molecular/atomic level—play a critical role in the properties and performance of a material. Hence, advanced machine cognition can effectively discern the interplay of complex microstructural features to assimilate structure-property-performance linkages, and design novel microstructures with engineered characteristics. Our team has demonstrated that AI can assimilate surrogate models for multiscale simulations, generate synthetic microstructures with controlled morphologies, learn linkages between geometry and physics, and design material microstructures for targeted properties. This project promises rich scientific advances in data driven design of next-generation EMs. Albeit the focus on EMs, foundational techniques and tools developed in this project are applicable to a broad range of complex materials.

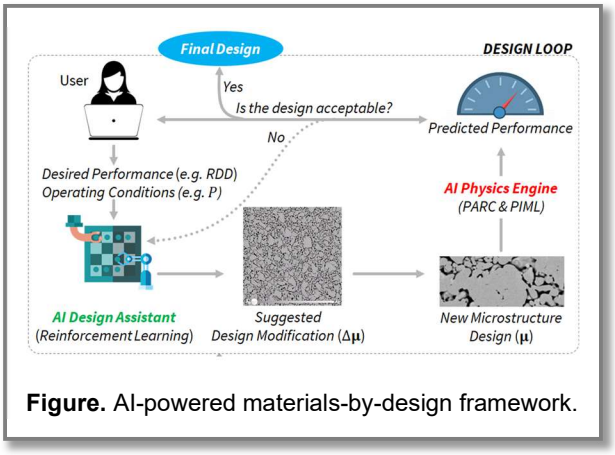


Figure. AI-powered materials-by-design framework.

Technical Progress

Prior to this DMREF project, our work was focused on a specific type of energetic material known as 'pressed Class V HMX.' The primary objective of this project is to establish mathematical and computational foundations to extend our previous findings to other types of energetic materials, including CL-20, TATB, RDX, and more. Since the inception of this project, we have amassed a substantial amount of reactive dynamics simulation data for these previously unstudied materials (Thrust 1). The SCIMITAR3D reactive dynamics code was employed to generate physics-based simulations of the shock initiation process of various species of energetic materials. The newly generated data were indexed and stored in a shared data storage accessible to the research team.

The new data has facilitated the development of meta-learning methods and raised new research questions (Thrust 2). One of the key research questions was how to utilize relatively inexpensive microscale (single pore collapse) simulation data to develop a new meso-/macro-scale (collapse of multiple pores) reactive dynamics model for an 'unseen' species of energetic material. To address this, we created a latent dynamics model named Latent-PARC, which builds upon our previous physics-aware recurrent convolutional neural network (PARC) reactive dynamics prediction model. Given single pore collapse simulation data, Latent-PARC encodes temperature fields, pressure fields, and microstructure geometry into a field of low-dimensional latent variables. The time evolution of these latent fields are then learned and modeled using PARC. The learned latent fields and the corresponding

dynamics yield a latent dynamics model corresponding to an individual pore at the microscale level. Now, at the meso-/macro-scale, where multiple pores are present, the single-pore latent dynamics model serves as an elementary representation of individual pore collapse modes, which can be integrated to build larger scale dynamics. Consequently, learning meso-/macro-scale dynamics is simplified from learning the entire reactive dynamics from scratch to modeling the interactions among individual pores, facilitating the learning process at the meso-/macro-scale where simulation data are significantly more expensive. In other words, with the Latent-PARC method, we are now capable of modeling the reactive dynamics of new energetic material species by using relatively inexpensive micro-scale simulation data together with a few meso-/macro-scale simulation samples.

Additionally, we are also exploring ways to transfer a model directly from one species of material to another. We are experimenting with different transfer- and meta-learning techniques to train a PARC model pre-trained on Class V HMX to a broader type of HMX like Classes I and III, as well as other organic energetic material species.

Meanwhile, we also made significant progress in developing the manufacturing capability for mock energetic materials using 3D printing. Now we are capable of fabricating materials with controlled microstructures. This will allow us to conduct physical experiments to measure the burn rate of mock materials as a function of different microstructures, and thereby the validation of computational and AI methods developed in this project.

To date, this project has produced 5 journal articles, 5 conference presentations, and 1 PhD dissertation.

Future Plans

We will continue to generate simulation data and to develop mathematical and computational underpinnings of meta-learning. Near the end of Year 3 or the beginning of Year 4, we will prioritize the burn experiments with 3D printed mock energetic materials, to enable the validation of meta-learning models against physical experiment data. Thus far, the meta-learning models have only been validated against simulation data, which may not align precisely with the real-world phenomena.

Broader Impacts and Workforce Development

A number of postdoctoral scholars (Drs. Phong Nguyen and Shahab Azarfar) and graduate students (Joseph Choi, Ranabir Saha, Pradeep Seshadri, and Levi Kirvy) were supported and/or participated in this project. Air Force NRO student, Jack Beerman, also participated in the project without compensation. We are closely collaborating with AFRL Eglin R/W on producing research workforce in the field of scientific machine learning.

We also are developing an interactive tutorial for PARC currently, for the engagement of broader communities. We anticipate the tutorial will be developed and ready near the end of Year 3. Building upon the tutorial, we will develop a half-day workshop for physics-informed machine learning.

Data Management and Open Access

Simulation data generated from this project are indexed and stored in a way that is findable and reusable. We are also building a Python data loader interface to make the data interoperable for different machine learning projects. Currently, the simulation data is not made accessible due to the sensitive nature of energetic materials. Other data generated from this project, such as software codes, are made available through our GitHub repository (https://github.com/stephenbaek/parc). Researchers can freely download the code and change/use it for their own needs. We are also in the process of developing easy-to-follow, interactive tutorial, walking through how to use PARC software codes for different material mechanics problems.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The new AI-powered materials-by-design loop will speed up material innovation significantly. Advanced machine cognition can effectively discern the interplay of complex microstructural features and design novel microstructures with engineered characteristics. For example, PARC can predict the evolution of temperature and pressure fields in shocked energetic materials with a comparable accuracy to direct numerical simulations (DNS), but multiple orders of magnitude faster computational speed—from days on a supercomputer for DNS to about a second on a personal workstation. This enables rapid evaluation of a wide variety of different microstructure designs without much computational overhead. Additionally, the development of an open-source library ‘MaterIQ’ will accelerate the AI integration in materials research by supplying advanced computational frameworks to discover, optimize, and design material systems multiple times faster and at a fraction of the cost.

Publications and References

1. Cheng, X., Nguyen, P. C. H., Seshadri, P. K., Verma, M., Gray, Z. J., Beerman, J. T., Udaykumar, H. S., Baek, S. (2024). Physics-aware recurrent convolutional neural networks for modeling multiphase compressible flows. *International Journal of Multiphase Flows*, In Press.
2. Choi, J. B., Nguyen, P. C. H., Sen, O., Udaykumar, H. S., & Baek, S. (2023). Artificial intelligence approaches for energetic materials by design: state of the art, challenges, and future directions. *Propellants, Explosives, Pyrotechnics, 48*(4), e202200276.
3. Nguyen, P. C. H., Nguyen, Y. T., Seshadri, P. K., Choi, J. B., Udaykumar, H. S., & Baek, S. (2023a). A Physics-Aware Deep Learning Model for Energy Localization in Multiscale Shock-To-Detonation Simulations of Heterogeneous Energetic Materials. *Propellants, Explosives, Pyrotechnics, 48*(4), e202200268.
4. Nguyen, P. C. H., Choi, J. B., Udaykumar, H. S., & Baek, S. (2023b). Challenges and opportunities for machine learning in multiscale computational modeling. *Journal of Computing and Information Science in Engineering, 23*(6), 060808.
5. Nguyen, P. C. H., Cheng, X., Azarfar, S., Seshadri, P. K., Nguyen, Y. T., Kim, M., ... & Baek, S. (2024). PARCv2: Physics-aware Recurrent Convolutional Neural Networks for Spatiotemporal Dynamics Modeling. In *Proceedings of the International Conference on Machine Learning (ICML 2024)*, Vienna, Austria.

Collaborative Research: DMREF: Switchable Underwater Adhesion through Dynamic Chemistry and Geometry

Lead Investigator: Michael D. Bartlett (mbartlett@vt.edu), Bruce P. Lee (bplee@mtu.edu), Rong Long (Rong.Long@colorado.edu), Grace X. Gu (ggu@berkeley.edu)
Participating Institutions: Virginia Tech, Michigan Tech, University of Colorado Boulder, University of California Berkeley
Website: https://dmref.org/projects/1577
Keywords: Adhesion, Soft materials, Mussel adhesive chemistry, Machine learning, Contact mechanics

Project Scope

We will combine dynamic underwater adhesive chemistry with active adhesive geometry to determine how adhesion can be switched in dry and wet conditions (Figure 1). This will be accomplished by incorporating mussel-inspired adhesive chemistry on an octopus-inspired adhesive structure to rapidly switch adhesion, which will allow us to simultaneously leverage the strengths of both organisms to develop new design principles to transform state-of-the-art adhesives. We will establish for the first time a switchable adhesive framework for cooperative design that amplifies the benefits of chemistry and active geometry for rapidly switchable yet strong underwater adhesives.

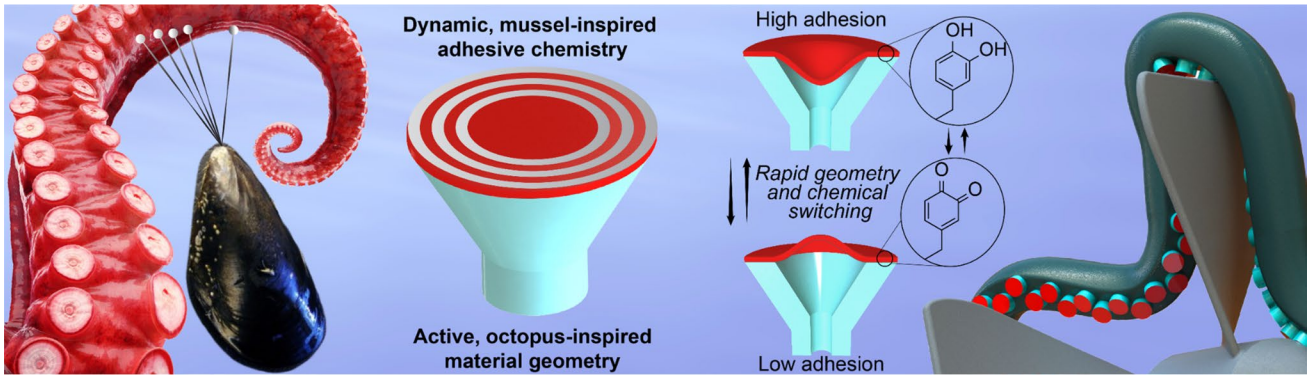


Figure 1. Project overview showing the mussel and octopus inspired switchable underwater adhesive

Relevance to MGI

Strong adherence to underwater or wet surfaces is a significant challenge, especially when rapid attachment with high capacity and easy release is required. To overcome this, we will systematically determine the geometry of the adhesive structure through feedback between mechanistic modeling and machine learning (ML) algorithms to create a virtual prototyping environment. This will feed into digital fabrication techniques to create materials and active membrane geometries enabling addressable and rapidly programmable adhesion strength. We will first determine the mechanisms behind octopus-inspired active geometry and mussel-inspired chemistry and then how they synergize to control adhesion. This provides unique opportunities to speed up the switching of adhesive chemistry by releasing the interface with active materials and enhancing the adhesion strength with engineered adhesive chemistry. Taken together, our approach will aim to simultaneously increase the switching ratio and strength of adhesion, and to reduce the switching time. By uniquely combining experiments, simulations, and ML, we will accelerate and build fundamental knowledge of how chemical, geometric, and material properties influence switchable adhesion to engineer rapidly switchable adhesives for wet and dry environments. We published a full team, joint review article on this proposed framework.[1]

Technical Progress

The team created a library of octopus-inspired adhesive with various geometries. We varied parameters such as the sample diameter, membrane thickness, outer stalk angle, wall thickness, and curvature of the adhesive surface to create 480 different unique sample configurations. This allows for a variety of experimental data points where

quantitative adhesion force was measured. We also added several features to improve measurement quality to better understand the mechanism of adhesion. This includes improved alignment, customized LEDs for better visualization, and a pressure gauge to measure the interfacial pressure between the active membrane and the substrate. The surface chemistry of the contacting membrane was also modified to create membrane surfaces that were either modified with mussel-inspired adhesives, adhesive molecules that could form hydrogen bonds with the surface substrate, or coatings with different levels of hydrophilicity. We found that the surface hydrophilicity has a bigger impact on the suction-based adhesion of octopus-inspired adhesives. To create an adhesive coating that could be controlled by applied electricity, an array of interdigitated electrodes (IDE) coated with mussel-inspired adhesive polymers. Contact mechanical testing indicates that the adhesive property could be reversibly controlled through changing the polarity of the electrodes.

The team has also developed finite element (FE) models to systematically investigate the effect of geometry on adhesion. We focused on developing a physics-based model for the suction effect of the octopus-inspired adhesive, while considering a thin layer of water trapped on the contact interface between the membrane and substrate. FE simulation matched adhesion results obtained experimentally. In addition, we also developed a set of analytical solutions for the adhesive contact between an inflated neo-Hookean membrane and a curved substrate, which is relevant to the low-adhesion state of the adhesive. A machine learning (ML) model and optimization platform were developed to test the FE model and provide feedback on the design variables and output parameters. We created a fully connected neural network that was trained on simulated data points with random adhesive geometries, which was able to determine the importance of individual variables that contributed to the adhesion performance. A neural network predictive model was trained to predict performances with given geometric parameters with reasonable accuracy, suggesting that the neural network surrogate model is reasonably accurate in predicting FE simulation results at an accelerated pace.

Future Plans

Objective 1 will determine how materials and geometry of an underwater adhesive element affect its adhesion performance against objects with different stiffness and curvature. We will establish fabrication techniques and characterization approaches, create mechanistic models, and use ML design over large geometric and material space. In Objective 2 we will elucidate the effect of chemistry patterning on the active membrane on the performance of underwater adhesion. Chemistry patterning will offer a new dimension of control over the adhesion strength and switching ratio by guiding the membrane detachment process against highly curved or soft substrate. This will create a library of catechol-based adhesives and predictive modeling tools for interface design that will leverage ML inverse design to accelerate pattern exploration. In Objective 3, we will combine dynamic adhesive chemistry with active membrane geometry for rapid and effective switchable adhesion. This includes electricity-controlled adhesion, using ML to determine coupling relationships between chemical patterns and geometry, and experimental implementation to determine the combined effect of active chemistry and geometry on adhesion switching ratio, switching time, and adhesion strength.

Broader Impacts and Workforce Development

In addition to training strong Ph.D. candidates, we will develop K-12 outreach activities by creating hands-on bioinspired adhesive robotic gripping kits and collaborating with programs such as Girls in Engineering and Society of Women Engineers. The Co-PI's will also each give online guest lectures in courses taught by the other members of the team. Adhesive design that combines strategies utilized by the octopus and mussel will be of great interests to a diverse group of students. We will develop a workshop at the Adhesion Society Annual Meeting to disseminate the concepts of ML and underwater adhesion. We will further host a career development panel and invite Adhesion Society members from academia, industry, national labs, and start-up companies as panelists to inform and inspire future workforce leaders in adhesion science and engineering.

Data Management and Open Access

Code for computational modeling and ML design and procedures for chemical and experimental operations will be released for public access as the project develops.

Advancing Along the Materials Development Continuum and Partnerships to Translation

As the project develops partnerships for translation will be explored to deploy the rapidly switchable underwater adhesives. Several invention disclosures have been submitted as groundwork for future translational efforts.

Publications and References

1. C. Lee, H. Shi, J. Jung, B. Zheng, K. Wang, R. Tutika, R. Long, B.P. Lee, G.X. Gu, and M.D. Bartlett, "*Bioinspired materials for underwater adhesion with pathways to switchability*" Cell Reports Physical Science, v.4 , 2023. DOI:10.1016/j.xcrp.2023.101597
2. M.D. Bartlett, S.W. Case, A.J. Kinloch, D.A. Dillard, "*Peel tests for quantifying adhesion and toughness: A review*" Progress in Materials Science, v.137, 2023. DOI: 10.1016/j.pmatsci.2023.101086
3. D. Hwang, C. Lee, X. Yang, J.M. Pérez-González, J. Finnegan, B. Lee, E.J. Markvicka, R. Long, M.D. Bartlett, "*Metamaterial adhesives for programmable adhesion through reverse crack propagation*" Nature Materials, v.22, 2023. DOI: 10.1038/s41563-023-01577-2
4. X. Yang, A. Srivastava, R. Long, "*Adhesive contact of an inflated circular membrane with curved surfaces*" International Journal of Solids and Structures, v.279, 2023. DOI: 10.1016/j.ijsolstr.2023.112371
5. S. Lee, Z. Zhang, G.X. Gu, "*Deep Learning Accelerated Design of Mechanically Efficient Architected Materials*" ACS Applied Materials & Interfaces, v.15, 2023. DOI: 10.1021/acsami.3c02746
6. Z. Jin, D.D. Lim, X. Zhao, M. Mamunuru, S. Roham, G.X. Gu, "*Machine learning enabled optimization of showerhead design for semiconductor deposition process*" Journal of Intelligent Manufacturing, 2023. DOI: 10.1007/s10845-023-02082-8
7. B. Zheng, C. Liu, Z. Li, C. Carraro, R. Maboudian, D.G. Senesky, G.X. Gu, "*Investigation of mechanical properties and structural integrity of graphene aerogels via molecular dynamics simulations*" Physical Chemistry Chemical Physics, v.25, 2023. DOI: 10.1039/D3CP02585C
8. K. Wang, L. Patra, B. Liu, Z. Zhang, R. Pandey, B.P. Lee, "*Salicylhydroxamic Acid as a Novel Switchable Adhesive Molecule*" Chemistry of Materials, v.35, 2023. DOI: 10.1021/acs.chemmater.3c00508
9. M.S. Bhuiyan, J. Manuel, R. Razaviamri, B.P. Lee, "*Electrochemical Deactivation of Switchable Catechol-Containing Smart Adhesive from Nonconductive Surfaces*" ACS Applied Polymer Materials, v.5, 2023. DOI: 10.1021/acsapm.3c00103
10. R. H. Plaut, D. Hwang, C. Lee, M. D. Bartlett, and D. A. Dillard "*Peeling of finite-length elastica on Winkler foundation until complete detachment*" International Journal of Solids and Structures, v. 256, 2022. DOI: 10.1016/j.ijsolstr.2022.111944
11. S.T. Frey, A.B. Haque, R. Tutika, E.V. Krotz, C. Lee, C.B. Haverkamp, E.J. Markvicka, M.D. Bartlett, "*Octopus-inspired adhesive skins for intelligent and rapidly switchable underwater adhesion*" Science Advances, v.8, 2022. DOI: 10.1126/sciadv.abq1905
12. B. Zheng, Z. Zheng, G.X. Gu, "*Designing mechanically tough graphene oxide materials using deep reinforcement learning*" npj Computational Materials, v.8, 2022. DOI: 10.1038/s41524-022-00919-z
13. D. Park, J. Jung, G.X. Gu, S. Ryu, "*A generalizable and interpretable deep learning model to improve the prediction accuracy of strain fields in grid composites*" Materials & Design, v.223, 2022. DOI: 10.1016/j.matdes.2022.111192
14. B. Zheng, Z. Zheng, G.X. Gu, "*Uncertainty quantification and prediction for mechanical properties of graphene aerogels via Gaussian process metamodels*" Nano Futures, v.5, 2021. DOI: 10.1088/2399-1984/ac3c8f
15. F. Razaviamri, S. Singh, J. Manuel, Z. Zhang, L.M. Manchester, C.L. Heldt, B.P. Lee, "*Utilizing Rapid Hydrogen Peroxide Generation from 6-Hydroxycatechol to Design Moisture-Activated, Self-Disinfecting Coating*" ACS Applied Materials & Interfaces, v.16, 2024. DOI: 10.1021/acsami.4c00213

DMREF: Complex Nanofeatures in Crystals: Theory and Experiment meet in the Cloud

Lead Investigator: Simon J. L. Billinge, sb2896@columbia.edu
Participating Institutions: Columbia University, University of Colorado
Source of Support: NSF-DMREF
Website: none
Keywords: quantum materials, broken local symmetry, DFT, pair distribution function analysis

Project Scope

The project aims to combine theory experiment and synthesis in a continuous loop to search for materials that exhibit intrinsic quantum textures, or local broken symmetries. These textures modify properties in non-trivial ways but are not detectable by traditional diffraction experiments or by traditional density functional theory (DFT) calculations. The hypothesis is that such materials are more common than previously thought, and can have valuable, sometimes enhanced, properties and by combining poly-DFT with synthesis and advanced atomic pair distribution function analysis (PDF) characterization measurements we can understand and discover new materials.

Relevance to MGI

Conventional DFT takes as input the crystal structure of a material and outputs the electronic structure, from which it is possible to infer properties such as whether a material is a metal, insulator, or magnetic. Sometimes DFT predicts the properties of a material to be something that is not seen experimentally. We recently showed that in many cases, if a model is used with a larger unit cell than seen crystallographically, broken local symmetries emerge which have lower energy than the average crystal structure. We call this approach polymorphous-DFT or poly-DFT. On the experimental side, PDF measurements, sensitive to local structure, also show a lower symmetry in the local structure than implied by the average crystal structure. The question arises whether this is a rare phenomenon or more widespread. Taking an MGI approach to predict polymorphous materials theoretically then to synthesize and characterize them with PDF then feed-back the information to guide new computational searches, we have sought to find new polymorphous materials.

Technical Progress

Progress has been rapid on the theory and experimental side. With theory we found previously unknown polymorphous behavior in a series of compounds [1, 2, 5, 6, 11, 15, 18], primarily perovskites ($LaTiO_3$, $LaVO_3$, $SrMnO_3$, $LaMnO_3$, $YNiO_3$, $BaTiO_3$) but also other compounds (FeSe, VO_2), a number of which were synthesized and measured using PDF where local structural distortions were observed

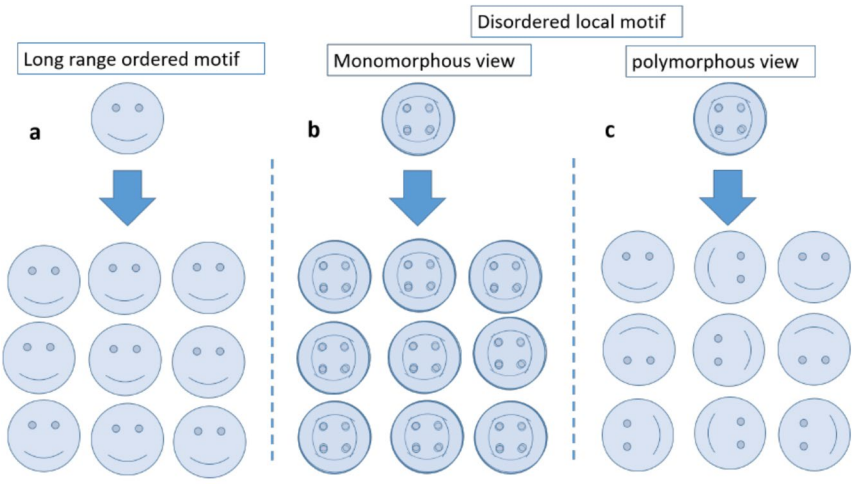


Figure. The top row shows the "average motif" obtained crystallographically. (a) the structure is long-range ordered (no local broken symmetry) and the local and average motifs are the same. (c) local motifs have broken symmetry but orientational disorder. The average motif is different from the local motif. (b) the naïve view if we assume long range order in the presence of the local broken symmetry. The local motif is wrong.

experimentally [11, 15, 18]. Of particular note, we identified as separation that the broken local symmetries can be in either structural or magnetic channels. (a) If the Local motifs are magnetic moments: an AFM long range order(LRO) can give band gap opening even though the average moment is zero leading naively to a metal; Also, even a PM phases can be an insulator if the moment distribution has some SRO. (b) If the local motifs are positional, such as bond disproportionation or Jahn-Teller distortions, the associated intrinsic symmetry breaking can change quantitatively the electronic structure. We made breakthroughs in the use of AI and machine learning in the difficult extraction of signals relating to local broken symmetry domains [7, 8, 9, 12, 14, 19, 20]. We developed a novel modeling method for finding coherent local structural distortions in perovskites from PDF data [13]. Finally, we also wrote, or contributed to, a number of review and overview papers [10, 16, 17] and a book [4] as part of the dissemination of the work some of which have already had high impact.

Future Plans

The collaboration has been highly successful and we are seeking follow-up funding to continue the work. Moving forward, beyond understanding the origin of polymorphousness and finding new polymorpous materials, we seek to understand how to *control* the textures as a materials design parameter to result in novel materials with tuned properties.

Broader Impacts and Workforce Development

Members of the DMREF team meet regularly by zoom and discuss progress and planning. Members are trained to write high quality reusable software, including documentation, which is released as open source software and widely used. As a result a number of former members have found jobs in the tech sector after leaving the project. The training and practice is done through the use of community open source coding practices including Use cases, unit testing and code review, handled through GitHub workflows. Mentorship of junior members in effective and ethical scientific practices is done by the senior members of the project. An outreach effort has been for PI Billinget to inject MGI principles and training into the JUAMI project that brings together US and East African students in two week schools [3].

Data Management and Open Access

All software, including machine learning models, that we have developed are released with open source licenses (BSD and CC0) through GitHub repositories. Trained models have also been deployed as cloud services at https://pdfitc.org. Much of the open source software we develop can be found through the Diffpy website at https://diffpy.org. For the ML models, the models used for training as well as trained models can be found at GitHub repositories that are linked to the supplementary materials of the relevant papers listed in the publication list.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The acceleration takes place through the coupling of poly-DFT, which is relatively quick, with sample synthesis which is the slow bottleneck. Poly-DFT can be run on many more materials than can be synthesized on the same timescale. We have found that the feedback is also essential. Whilst DFT can predict materials that might be interesting polymorphous targets, it does not predict synthesizability, and so a feedback loop where synthesizability issues coming from solid-state chemists guides the search domain of the DFT which then predicts polymorphousness in that materials domain.

Publications and References

1. Xiuwen Zhang, Jia-Xin Xiong, and Alex Zunger. “The emergence of split-off flat bands and hidden magnetism in the insulator-metal transition in VO_2”. In: *npj Computational Materials* (2024). submitted 2024

2. Jia-Xin Xiong, Xiuwen Zhang, and Alex Zunger. “Symmetry breaking forms split-off flat bands in quantum oxides controlling metal versus insulator phases”. *PRX* (2024), submitted

3. Simon J. L. Billinge. “JUAMI, the joint undertaking for an African materials institute: building materials science research collaborations and capabilities between continents”. In: *Acta Crystallographica: Section E* **80**.2 (2024), pp. 102–105. doi: 10.1107/S2056989023010915.

4. Simon J. L. Billinge and Kirsten Jensen. *Atomic pair distribution function analysis: a primer*. Oxford: Oxford University Press, 2024.

5. Oleksandr I. Malyi and Alex Zunger. “Rise and fall of Mott insulating gaps in $YNiO_3$ paramagnets as a reflection of symmetry breaking and remaking”. *Physical Review Materials* **7**, 044409 (2023). DOI: 10.1103/PhysRevMaterials.7.044409

6. Oleksandr I. Malyi, Xin-Gang Zhao, and Alex Zunger. “Insulating band gaps both below and above the Néel temperature in d-electron $LaTiO_3$, $LaVO_3$, $SrMnO_3$, and $LaMnO_3$ perovskites as a symmetry-breaking event”. *Physical Review Materials* **7**, 074406 (2023). DOI: 10.1103/PhysRevMaterials.7.074406

7. Emil T. S. Kjær, Andy S. Anker, Marcus N. Weng, Simon J. L. Billinge, Raghavendra Selvan, and Kirsten M. Ø. Jensen. “DeepStruc: Towards structure solution from pair distribution function data using deep generative models”. In: *Digital Discovery* **2** (2023), pp. 69–80. doi: 10.1039/D2DD00086E. url: https://doi.org/10.1039/D2DD00086E

8. Andy S. Anker, Ulrik Friis-Jensen, Frederik L. Johansen, Simon J. L. Billinge, and Kirsten M. Ø. Jensen. “ClusterFinder: A fast tool to find cluster structures from pair distribution function data”. In: *Acta Crystallogr. A* **80**.2 (2023), pp. 213–220. doi: 10.1107/S2053273324001116.

9. Ran Gu, Simon J. L. Billinge, and Qiang Du. “A fast two-stage algorithm for non-negative matrix factorization in smoothly varying data”. In: *Acta Crystallogr.: Section A* **79**.2 (2023), pp. 203–216. doi: 10.1107/S2053273323000761. url: https://onlinelibrary.wiley.com/iucr/doi/10.1107/S2053273323000761

10. Zunger, A. “Bridging the gap between density functional theory and quantum materials”. *Nat. Comput. Sci*. **2**, 529-532 2022

11. Zhao, X. G., Malyi, O. I., Billinge, S. J. L., & Zunger, A. “Intrinsic local symmetry breaking in nominally cubic paraelectric $BaTiO_3$.” *Phys. Rev. B* **105**, 224108 (2022)

12. Andy S. Anker, Emil T. S. Kjær, Mikkel Juelsholt, Troels Lindahl Christiansen, Susanne Linn Skjærvø, Mads Ry Vogel Jørgensen, Innokenty Kantor, Daniel Risskov Sørensen, Simon J. L. Billinge, Raghavendra Selvan, and Kirsten M. Ø. Jensen. “Extracting structural motifs from pair distribution function data of nanostructures using explainable machine learning”. In: *npj Computational Materials* **8** (2022), p. 213. doi: 10.1038/s41524-022-00896-3.

13. Sandra H. Skjaervoe, Martin A. Karlsen, Riccardo Comin, and Simon J. L. Billinge. “Refining perovskite structures to pair distribution function data using collective Glazer modes as a basis”. In: *IUCrJ* **9**.5 (2022), pp. 705–712. doi: 10.1107/S2052252522007680.

14. Emil T. S. Kjær, Olivia Aalling-Frederiksen, Long Yang, Nancy K. Thomas, Mikkel Juelsholt, Simon J. L. Billinge, and Kirsten M. Ø. Jensen. “In situ studies of the formation of tungsten and niobium oxide nanoparticles: Towards automated analysis of reaction pathways from PDF analysis using the Pearson correlation coefficient”. In: *Chemistry Methods* **2**.9 (2022), e202200034. doi: 10.1002/cmtd.202200034. url: https://doi.org/doi.org/10.1002/cmtd.202200034

15. Xin-Gang Zhao, Oleksandr I. Malyi, Simon J.L. Billinge, and Alex Zunger. “Intrinsic local symmetry breaking in the nominally cubic paraelectric phase of $BaTiO_3$”. In: *Phys. Rev. B* **105** (2022), p. 224108. doi: 10.1103/PhysRevB.105.224108.

16. Kamal Choudhary, Brian DeCost, Chi Chen, Anubhav Jain, Francesca Tavazza, Ryan Cohn, Cheol WooPark, Alok Choudhary, Ankit Agrawal, Simon J. L. Billinge, Elizabeth Holm, Shyue Ping Ong, and Chris Wolverton. “Recent Advances and Applications of Deep Learning Methods in Materials Science”. In: *npj Comput Mater* **8** (2022), p. 59. doi: 10.1038/s41524-022-00734-6.

17. Eric A. Stach, Brian DeCost, A. Gilad Kusne, Jason Hattrick-Simpers, Keith A. Brown, Kristofer G. Reyes, Joshua Schrier, Simon J. L. Billinge, Tonio Buonassisi, Ian Foster, Carla P. Gomes, John M. Gregoire, Apurva Mehta, Joseph Montoya, Elsa Olivetti, Chiwoo Park, Eli Rotenberg, Semion K. Saikin, Sylvia Smullin, Valentin Stanev, and Benji Maruyama. “Autonomous experimentation systems for materials development: A community perspective”. In: *Matter* **4**.9 (2021), pp. 2702–2726. doi: 10.1016/j.matt.2021.06.036.

18. Zhi Wang, Xin-Gang Zhao, Robert Koch, Simon J. L. Billinge, and Alex Zunger. “Understanding electronic peculiarities in tetragonal FeSe as local structural symmetry breaking”. In: *Phys. Rev. B* **102**.23 (2020), p. 235121. doi: 10.1103/PhysRevB.102.235121.

19. Andy S. Anker, Emil T. S. Kjaer, Erik B. Dam, Simon J. L. Billinge, Kirsten M. Ø. Jensen, and Raghavendra Selvan. “Characterising the atomic structure of mono-metallic nanoparticles from x-ray scattering data using conditional generative models”. In: *KDD* (2020). Accepted to the conference International Workshop on Deep Learning on Graphs (KDD-DLG). Available on ChemArxiv (doi is 10.26434/chemrxiv.12662222). doi: 10.26434/chemrxiv.12662222.

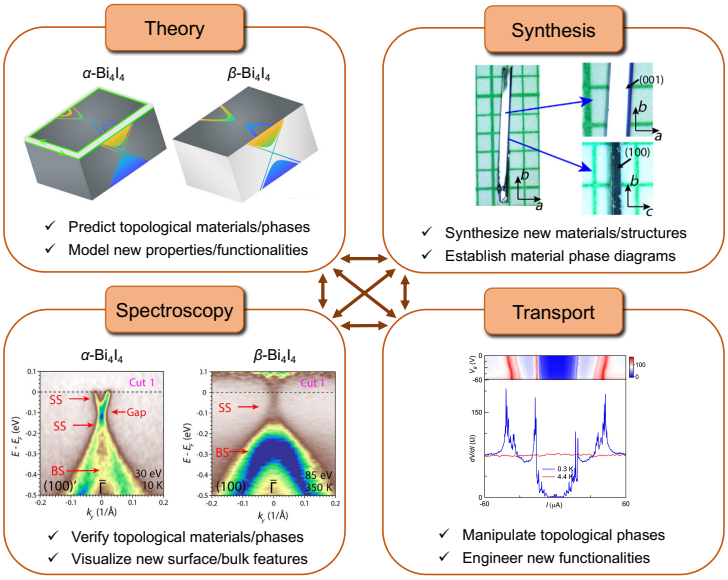
20. Emil T. S. Kjær, Olivia Aalling-Frederiksen, Long Yang, Nancy K. Thomas, Mikkel Juelsholt, Simon J. L. Billinge, and Kirsten M. Ø. Jensen. “In situ studies of the formation of tungsten and niobium oxide nanoparticles: Towards automated analysis of reaction pathways from PDF analysis using the Pearson correlation coefficient”. In: *Chemistry Methods* **2**.9 (2022), e202200034. doi: 10.1002/cmtd.202200034.

DMREF Collaborative Research: Developing and Harnessing the Platform of Quasi-One-Dimensional Topological Materials for Novel Functionalities and Devices

Principal Investigators: R. J. Birgeneau[1], C. N. Lau[2], Bing Lv[3], Ming Yi[4], Fan Zhang[3]
Participating Institutions: 1. UC Berkeley, 2. Ohio State Univ., 3. UT Dallas, 4. Rice Univ.
Website: https://dmref-q1dtm.wixsite.com/home/team **Twitter:** q1dtm
Keywords: topological insulator, quasi-one-dimensional material, device

Project Scope

Our research scope includes discovering new quasi-1D topological materials, creating their atomic layers and moirés, manipulating their topological phases transitions, realizing devices and functionalities for new technologies. This project advances the discovering and utilization of quasi-1D topological materials, building on our leadership position in this field, the established iterative feedback loop among theory, synthesis, characterization, and devices, and the significant new research directions and device concepts emergent from our prior DMREF project. The new knowledge and database to be established will prepare future scientists to discover, invent, and innovate. Our educational activities integrated into the research include increasing the participation of the underrepresented groups, performing public outreach, mentoring undergraduate and REU students, and comprehensive training of students and postdocs.



Relevance to MGI

To achieve the goal of efficient discovery and optimization of topological materials, our program operates on an iterative feedback loop from theoretical prediction of topological materials to crystal synthesis to electronic structure characterization to transport realization via device fabrication back to inputs for better theoretical modeling. One successful example is our identification of the monolayers of Bi_4I_4 and Bi_4Br_4 as 2D topological insulators (TI), serving as the building blocks for constructing various topological phases realized via different stacking orders of such layers in real materials $Bi_4I_{4-x}Br_x$ ($0 \le x \le 4$). From this design principle, we have theoretically predicted and experimentally verified a few rare topological phases in bismuth halides, including weak TI, higher-order TI, and large-gap 2D TI. The success of the feedback loop is especially evidenced by our recent realization of an ideal weak TI (x=2.8), where the complete set of topological surface state of a pair of Dirac cones and the helical saddle points connecting them are optimized to be exposed in a large global bulk gap at all temperatures. It is impossible to efficiently discover or optimize this weak TI without the iterative feedback loop.

Technical Progress

We established a complete structural and topological phase diagram for the $Bi_4I_{4-x}Br_x$ ($0 \le x \le 4$) family, with new structures and band topologies identified. In particular, the x=2.8 case represents an ideal weak TI, as shown by our ARPES experiment and first-principles calculation. In addition, we have successfully synthesized a dozen of other high-quality quasi-1D materials and carried out exploratory syntheses with new quasi-1D materials and structures identified. These include $TaTe_4$, $NbTe_4$, $(TaSe_4)_2I$, $NbTe_4I$, $TaTe_4I$, $K_2Mo_3As_3$, $Rb_2Mo_3As_3$, $Cs_2Mo_3As_3$, Nb_4FeTe_4, $BaFe_2Se_4$, Ba_2FeSe_3, $Ba_9Fe_4Se_{16}$, $Ba_5Fe_9S_{18}$, $K_3Fe_2Se_4$, $BaPt_4Se_6$, $Zr_{6.5}Pt_6Se_{19}$, β-$BaCu_2As_2$, $BaCu_6Sn_2As_{4-x}$, $BaCu_6Sn_2P_{4-x}$, and Verbeekite-$PdSe_{1.2}Te_{0.8}$.

We nanofabricated ultrathin Bi_4I_4 and Bi_4Br_4 devices and observed gate-tunable longitudinal/Hall resistances. We further achieved a Bi_4I_4 Josephson junction and observed a gate-tunable supercurrent. We predicted that

Bi_4I_4/Bi_4Br_4 atomic layers offer a unique platform toward achieving room-temperature quantum spin Hall (QSH) effect and topological many-body physics. Together with our collaborators, we showed that the atomic layers of Bi_4I_4 and Bi_4Br_4 could exhibit room-temperature QSH effect. In particular, a scanning tunneling microscopy (STM) study provided compelling evidence for such QSH step-edge states that persisted to 300 K.

Additionally, our team made several other significant contributions to the field of quantum materials. The fabrication challenges and emergent physics of moiré materials were critically reviewed, and a quantum geometric mechanism for understanding and designing flat-band superconductors was distilled. New correlated phases driven by van Hove singularities were identified in Kagome metals and AB bilayer graphene. Intelligent optical sensing enabled by quantum geometry was co-invented and patented. New 2D magnetic materials with high Curie temperatures and topological excitations were discovered.

Future Plans

(i) We will continue to predict, synthesize, characterize, and optimize quasi-1D topological materials. (ii) We will engineer, discover, and control possible topological phase transitions in these materials. (iii) We will create and explore quasi-1D topological materials in atomically thin limit and moiré superlattices. (iv) We will nanofabricate their devices toward realizing room-temperature quantum spin Hall insulators and intelligent photodetectors. (v) We will document all our new quasi-1D topological/correlated materials data to our DMREF website. (vi) Our team will produce short videos, made free in our YouTube channel, on formation of single crystals in a furnace, a day working at the national synchrotron facilities, methods of exfoliating and stacking 2D atomic layers, and learning to recognize crystalline symmetries. (vii) We will continue and strengthen our efforts in involving undergraduate and REU students to our DMREF project, particularly those from the under-represented groups.

Broader Impacts and Workforce Development

We have demonstrated $Bi_4I_{4-x}Br_x$ ($0 \le x \le 4$) as a unique tunable material platform for exploring the rich interplay of geometry, symmetry, topology, and interaction – a fundamental theme of physics. Significantly, they not only ideally realize multiple topological phases that are otherwise inaccessible but also manifest novel electronic properties and device concepts, thereby accelerating the discovery of a new generation of topological materials for novel functionalities and devices. In the January of 2023, we organized a two-day virtual workshop, *Q1D Topological Quantum Materials*, and all the talks were documented in our free Youtube channel.

An integral effort of our program is the education and training of graduate and undergraduate students as well as career preparation for postdocs. For example, nine students obtained their physics Ph.D., including one female, one LGBT, and two recipients of the Steven Weinberg Research Awards from the Texas Section of American Physical Society. Additionally, one REU student was awarded an NSF Graduate Research Fellowship, and two students received internships from the Air Force Research Lab and Sandia National Lab. Our regular interactions between the five groups provide junior participants a broad training covering materials chemistry and synthesis, materials physics and characterizations, and materials modeling and predictions. In addition, PI Birgeneau has created a new endowed program and a new endowed fund for underrepresented students at UC Berkeley.

Data Management and Open Access

Our research results have been disseminated to the research communities through journal publications, Ph.D. dissertations, and conference presentations. In addition to free versions online, all these are available from us upon request. We are documenting all our quasi-1D topological materials data from both experiment and computation to our DMREF website and making them searchable and free.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Operating on an iterative closed loop from theoretical prediction to crystal synthesis to material characterization to device functionality back to inputs for better theoretical modeling, we have efficiently discovered and optimized new topological materials in the $Bi_4I_{4-x}Br_x$ ($0 \le x \le 4$) family and other quasi-1D families. We have established the physics platform and materials database of these quasi-1D materials that sidestep the shortcomings of quasi-2D van der Waals materials, and further developed them along the Material Development Continuum for emergent materials, functionalities, and devices toward technology applications. Particularly, leveraging our success in the bismuth halides, we are creating their monolayers and moiré superlattices for engineering novel devices enabled by their large, tunable, topological band gaps and by our recently demonstrated intelligent infrared sensing.

Our Publications (*12 Most Closely Related and Other Significant Publications since the 2022 Meeting*)

1. T. Han, Z. Lu, Y. Yao, J. Yang, J. Seo, C. Yoon, K. Watanabe, T. Taniguchi, L. Fu, F. Zhang, and L. Ju, *Large quantum anomalous Hall effect in spin-orbit proximitized rhombohedral graphene*, Science **384**, 647-651 (2024).
2. F. Winterer, F. R. Geisenhof, N. Fernandez, A. M. Seiler, F. Zhang, and R. T. Weitz, *Ferroelectric and spontaneous quantum Hall states in intrinsic rhombohedral trilayer graphene*, Nat. Phys. **20**, 422-427 (2024).
3. Y. Zhang, H. Tian, H. Li, C. Yoon, R. A. Nelson, Z. Li, K. Watanabe, T. Taniguchi, D. Smirnov, R. K. Kawakami, J. E. Goldberger, F. Zhang, and C. N. Lau, *Quantum octets in high mobility pentagonal two-dimensional PdSe2*, *Nat. Commun.* **15**, 761 (2024).
4. D. Shcherbakov, G. Voigt, S. Memaran, G.-B. Liu, Q. Wang, K. Watanabe, T. Taniguchi, D. Smirnov, L. Balicas, F. Zhang, and C. N. Lau, *Giant tunability of intersubband transitions and quantum Hall quartets in few-layer InSe quantum well*, Nano Lett. **24**, 3851–3857 (2024).
5. J. S. Oh, T. Xu, N. Dhale, S. Li, C. Lei, C. Yoon, W. Liu, J. Huang, H. Wu, M. Hashimoto, D. Lu, C. Jozwiak, A. Bostwick, E. Rotenberg, C. N. Lau, B. Lv, F. Zhang, R. J. Birgeneau, and M. Yi, *Ideal weak topological insulator and protected helical saddle points*, Phys. Rev. B **108**, L201104 (2023).
6. X. Teng, J. S. Oh, H. Tan, L. Chen, J. Huang, B. Gao, J.-X. Yin, J.-H. Chu, M. Hashimoto, D. Lu, C. Jozwiak, A. Bostwick, E. Rotenberg, G. E. Granroth, B. Yan, R. J. Birgeneau, P. Dai, and M. Yi, *Intertwined magnetism and charge density wave order in kagome FeGe*, Nat. Phys. **19**, 814-822 (2023).
7. S. Yuan, C. Ma, E. Fetaya, T. Mueller, D Naveh, F. Zhang, and F. Xia, *Geometric deep optical sensing*, Science **379**, eade1220 (2023).
8. H. Tian, S. Che, T. Xu, P. Cheung, K. Watanabe, T. Taniguchi, M. Randeria, F. Zhang, C. N. Lau, and M. W. Bockrath, *Evidence for Dirac flat band superconductivity originating from quantum geometry*, Nature **614**, 440 (2023).
9. N. Shumiya, M. S. Hossain, J.-X. Yin, Z. Wang, M. Litskevich, C. Yoon, Y. Li, Y. Yang, Y.-X. Jiang, G. Cheng, Y.-C. Lin, Q. Zhang, Z.-J. Cheng, T. A. Cochran, D. Multer, X. P. Yang, B. Casas, T.-R. Chang, T. Neupert, Z. Yuan, S. Jia, H. Lin, N. Yao, L. Balicas, F. Zhang, Y. Yao, M. Z. Hasan, *Evidence of a room-temperature quantum spin Hall edge state in a higher-order topological insulator*, Nat. Mater. **21**, 1111 (2022).
10. W. Liu, X. Guo, J. Schwartz, H. Xie, N. U. Dhale, S. H. Sung, A. L. N. Kondusamy, X. Wang, H. Zhao, D. Berman, R. Hovden, L. Zhao, and B. Lv, *A three-stage magnetic phase tran- sition revealed in ultrahigh-quality van der Waals bulk magnet CrSBr*, ACS Nano **16**, 15917-15926 (2022).
11. X. Chen, E. Schierle, Y. He, M. Vranas, J. W. Freeland, J. L. McChesney, R. Ramesh, R. J. Birgeneau, and A. Frano, *Antiferromagnetic order in Co-doped Fe5GeTe2 probed by resonant magnetic x-ray scattering*, Phys. Rev. Mater. **6**, 094404 (2022).
12. X. Chen, Y.-T. Shao, R. Chen, S. Susarla, T. Hogan, Y. He, H. Zhang, S. Wang, J. Yao, P. Ercius, D. A. Muller, R. Ramesh, and R. J. Birgeneau, *Pervasive beyond Room-Temperature Ferromagnetism in a Doped van der Waals Magnet*, Phys. Rev. Lett. **128**, 217203 (2022).

DMREF: Discovery of unconventional superconductors by design

Lead Investigator: Antia Botana, asanc157@asu.edu and Julia Mundy, mundy@fas.harvard.edu
Co-PIs: Jenny Hoffman, jhoffman@g.harvard.edu and Jarad Mason, mason@chemistry.harvard.edu
Participating Institutions: Arizona State University and Harvard University
Source of Support: NSF-DMREF (DMR-2323970)
Website: None yet
Keywords: Superconductors, nickelates, molecular beam epitaxy, density functional theory

Project Scope

This DMREF project will accelerate the discovery of new superconducting materials through a multi-disciplinary team that unites experience in materials synthesis, local probes, and computation. We seek to: 1) Predict new materials candidates for unconventional or high-temperature superconductivity and validate materials descriptors; 2) Develop synthetic pathways to apply soft chemistry to thin films and construct mixed anion thin films predicted to display high-temperature superconductivity (HTS); 3) Probe local structural, electronic, and magnetic properties and take advantage of nanoscale heterogeneity to correlate local descriptors with the superconducting critical temperature (T_c) in novel superconductors; 4) Develop AI-ready experimental and computational datasets on candidate superconductors and 5) Train a diverse set of scholars on interdisciplinary materials-by-design.

Relevance to MGI

We will accelerate the discovery of new superconducting materials through a multi-disciplinary team that unites experience in materials synthesis, local probes, and computation. This tight coupling between theory and experiment is possible only in the context of a DMREF and it follows the program laid out in the Materials Genome Initiative for Global Competitiveness (MGI). To design, simulate, and accelerate the discovery of new superconductors we will use computational tools including density functional theory (DFT) and dynamical mean field theory (DMFT) to predict both the crystal and electronic structures of candidate correlated electron materials and high temperature superconductors. The most promising predicted materials will then be synthesized by combining two traditionally disparate forms of materials synthesis for the first time -- advanced thin film deposition by reactive oxide MBE and low-temperature soft chemistry -- to make metastable materials that could not previously be realized. The materials will then be interrogated by bulk and local probes to map resistivity, structure, orbital polarization/hybridization, phonons, and spin interactions. Our approach closes the loop between the prediction of materials with our descriptors and direct measurement of these properties. The resulting large datasets will be AI-ready and can be correlated to build structure-property relationships.

Technical Progress

During this year, we have made significant progress on Thrust 1 ('Search for HTS in Nickelates and other d^9 materials') by:

1) Answering a key open question in the study of layered superconducting nickelate films: the role that hydrogen incorporation into the lattice plays in the appearance of the superconducting state. Using secondary ion mass spectrometry on superconducting films grown by co-PI Mundy, no evidence for extensive hydrogen incorporation has been found. Theoretical calculations by co-PI Botana corroborated that hydrogen incorporation is broadly energetically unfavorable in these systems. In this manner, our combination of theory and experiment has shown that hydrogen incorporation is not required to achieve a superconducting state in layered square-planar nickelates. This conclusion will greatly help our team moving forward in the soft chemistry approaches required for part of our project.
2) Expanding the superconducting square planar nickelate family beyond the infinite-layer and quintuple layer members of the $R_{n+1}Ni_nO_{2n+2}$ family (R= rare-earth, n= number of NiO_2 layers). In work that is currently in

preparation, our theory+experiment approach has shown that all members of the Nd-based layered nickelate family from n=4 to n=8 are superconducting with a dome-like dependence of T_c with n.

Future Plans

The most immediate plans for the project are related to: i) anion substitution in nickelates of the layered $R_{n+1}Ni_nO_{2n+2}$ family and ii) expansion of superconducting d^9-like systems beyond nickelates to palladates. For the anion exchange reactions we will investigate the possibility of altering the electronic structure of low-n layered nickelate materials by incorporating fluorine. We hypothesize that the degree of orbital polarization can be increased due to the change in electronegativity and, if the desired doping level (corresponding to ~$d^{8.8}$ filling) can be achieved, a higher T_c can then also be expected. We will focus on expanding the family of fluoro-nickelates performing similar theoretical studies to those performed in nickelates in our prior collaboration. For the palladates, we will study the whole palladate analog family to the $R_{n+1}Ni_nO_{2n+2}$ nickelates. We hypothesize that a hole-doped d^9 electronic configuration on a square lattice with a dominant $d_{x^2-y^2}$ orbital at the Fermi level is a common thread of superconducting families in proximity to d^9 filling for the corresponding transition metal ion. Our DFT computations of the crystal and electronic structures of the infinite-layer palladate $LaPdO_2$ show that palladate compounds are somewhere in-between cuprates and nickelates – with a single-band $d_{x^2-y^2}$ Fermi surface topology. Experimentally, we will first study this compound and subsequently expand to other n values of the series, combining theory and experiment. In contrast to the nickelates, it may be possible to synthesize the palladates directly in the square-planar format due to the stability of Pd^{1+} in contrast to Ni^{1+}. Initial films will be imaged using magnetic force microscopy (MFM) for patches of diamagnetism indicative of superconductivity; refined films with flatter surfaces will be imaged using scanning tunneling microscopy and spectroscopy to elucidate the electronic structure of novel superconductivity.

Broader Impacts and Workforce Development

This program will support 3 experimental graduate students at Harvard and 2 students performing electronic structure calculations at ASU. The students will grow into experimentalists who can synthesize and measure, but also understand the principles of materials design; or theorists who can predict new materials, but also interpret data from their experimental collaborators. This interdisciplinary training will promote the cultural change that is required to address the challenges posed by the rapid development and specialization of modern science and technology. We are incorporating high school and undergraduate researchers in pedagogical and useful projects to code, test electronics, and to develop automated chemical etching procedures for atomically-sharp high-symmetry probe tips for microscopic imaging of synthesized materials.

Data Management and Open Access

Our materials discovery and design strategy complies with the MGI and DMREF recommendations to ensure both data storage and access. Our goals are to: i) Make materials data open, accessible, and useful. ii) Provide researchers with a platform to organize materials data. iii) Create a data-themed community of researchers. We will use the MongoDB and zenodo platforms as well as the project research website to make data open and accessible (the project website is currently under development).

Advancing Along the Materials Development Continuum and Partnerships to Translation

This project will accelerate the development of new high-T_c superconductors and hence realize their potential for proposed applications ranging from energy storage/generation to quantum computing. Using our computational tools we will filter materials possibilities and propose the most promising candidates for efficient experimental realization, in an approach that has already worked in our team. In this manner, we will accelerate the arrival of technology-ready materials at a fraction of the time and cost that would have been necessary to explore the full space experimentally. The development of AI-ready experimental and computational datasets on candidate superconductors will also enable achieving this goal.

Publications and References

1. Purnima P. Balakrishnan, Dan Ferenc Segedin, Lin Er Chow, P. Quarterman, Shin Muramoto, Mythili Surendran, Ranjan K. Patel, Harrison LaBollita, Grace A. Pan, Qi Song, Yang Zhang, Ismail El Baggari, Koushik Jagadish, Yu-Tsun Shao, Berit H. Goodge, Lena F. Kourkoutis, Srimanta Middey, Antia S. Botana, Jayakanth Ravichandran, A. Ariando, Julia A. Mundy and Alexander J. Grutter, *Hydrogen is not necessary for superconductivity in topotactically reduced nickelates,* arXiv:2403.01796 (2024). DOI: 10.48550/arXiv.2403.01796
2. Harrison LaBollita, Soumen Bag, Jesse Kapeghian, and Antia S. Botana *Electronic correlations, layer distinction, and electron doping in the alternating single-layer trilayer $La_3Ni_2O_7$ polymorph,* arXiv.2404.19089 (2024) DOI: 10.48550/arXiv.2404.19089
3. Harrison LaBollita, Jesse Kapeghian, Michael R. Norman, and Antia S. Botana, *Electronic structure and magnetic tendencies of trilayer $La_4Ni_3O_{10}$ under pressure: Structural transition, molecular orbitals, and layer differentiation,* Physical Review B **109**, 195151 (2024), DOI: 10.1103/PhysRevB.109.195151

DMREF: GOALI: Tetrahedral Ferroelectrics

Lead Investigator: Geoff Brennecka, geoff.brennecka@mines.edu
Participating Institutions: Colorado School of Mines, Penn State University, Carnegie Mellon University, Broadcom, National Renewable Energy Lab (unfunded)
Source of Support: NSF-DMREF
Website: none
Keywords: Ferroelectrics, Wurtzite, Domain Walls, Sputtering

Project Scope

The premise of this project is to better understand the nature of tetrahedrally-based ferroelectrics and to expand this family of materials beyond the original (Al,Sc)N and (Zn,Mg)O. We aim to answer the following 3 questions:

1) How do switchable polarization, coercive field, stiffness, a paraelectric transition, and structure interrelate?
2) What are the switching mechanism(s)?
3) How do local structure, point defects, and synthesis affect switching and breakdown?

We have made substantial progress towards 2 and 3, and these are feeding gradual progress towards question 1.

Relevance to MGI

Our project integrates DFT-based calculations, reactive sputter growth, electrical measurements, and structural / chemical characterization using x-ray and electron microscopy techniques. We have successful examples of experiment leading theory/modeling (e.g., defects in (Al,Sc)(O,N)), models guiding experiment (prediction and realization of new compounds and alloys such as (Al,Gd)N), and measurements driving a revision of earlier thinking and interpretation of both theory and experiments (e.g., extending a classic model of domain switching kinetics). Key to this success is the close collaboration and aligned intellectual contribution from all team members regardless of background or tool(s) of choice.

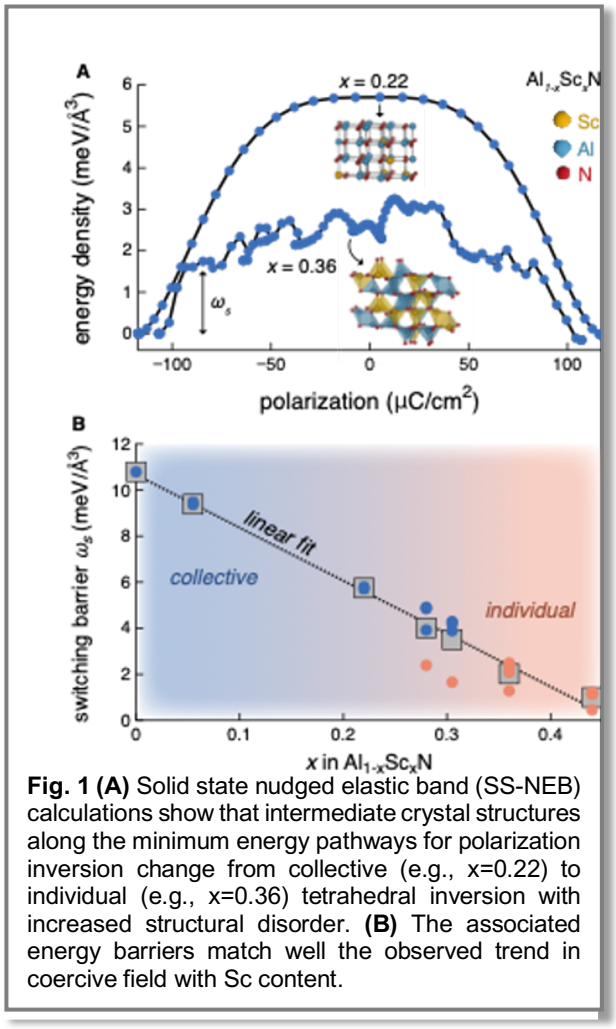


Fig. 1 (A) Solid state nudged elastic band (SS-NEB) calculations show that intermediate crystal structures along the minimum energy pathways for polarization inversion change from collective (e.g., x=0.22) to individual (e.g., x=0.36) tetrahedral inversion with increased structural disorder. **(B)** The associated energy barriers match well the observed trend in coercive field with Sc content.

Technical Progress

The large coercive fields (E_c) and extremely square polarization-vs-field (PvsE) loops are consistent with polarization reversal being a high-energy process. We showed experimentally how the abruptness of this transition fails to follow the classic Kolmogorov-Avrami-Ishibashi (KAI) switching kinetics model, but more importantly, that if one relaxes the assumptions of the original KAI model to allow simultaneous growth and increasing nucleation rate, we can capture both nucleation and growth dynamics across a broader range of scenarios than KAI while collapsing to the identical description under the originally-assumed boundary conditions. This insight and subsequent mathematical description has been used to explain the both the abrupt polarization reversal seen in wurtzite ferroelectrics and, combined with theory-guided experiments, the previously-baffling wake-up phenomena widely reported for these materials.

Computation has guided both the identification (prioritization) of new compositional spaces for study and

the mechanistic understanding of the polarization inversion process itself. One example of this is the identification of a clear change polarization switching processes with increasing structural disorder. Using the prototypical (Al,Sc)N alloy as an example, in pure AlN and alloys with low Sc content, the cation-centered tetrahedra invert collectively, associated with a single large energy barrier. The disorder associated with increasing Sc content enables individual tetrahedra to invert sequentially, with each such inversion necessitating a smaller incremental energy input and leading to a lower overall coercive field for the alloy. This aligns well with experimental coercive field and remanent polarization data from our group as well as the extensive literature on (Al,Sc)N alloys (Fig. 1). We have extended this concept across promising candidate compounds and identified design rules for initiating such individual switching pathways, and have even demonstrated a direct application of this concept in predicting and then experimentally validating composition-dependence of coercive field in (Al,Gd)N.

Future Plans

In the remainder of our project, we are continuing to explore new compounds and alloys while extending our efforts related to defects and defect compensation in these wurtzites. We are starting with more detailed studies on the effects of ubiquitous oxygen contamination in (Al,Sc)N, particularly related to charge carrier concentration and domain walls, and then extending this work to other non-stoichiometric chemistries. Such studies are particularly important for quantitatively linking computational and experimental results, because real samples are never as perfect as models assume them to be.

Broader Impacts and Workforce Development

This project is serving as a nucleus around which other related efforts have connected such that the MGI mindset permeates the groups involved well beyond the students supported directly by this project. The MGI approach is integrated into both undergraduate and graduate courses across the three academic institutions, including the newly launched Ceramic Engineering BS program at Mines which bakes in a joint computational / experimental approach from the start. While there is only a single undergraduate course focused on computation itself, discussions and hands-on use of combined computational and experimental approaches permeate all courses and labs. The PIs and students on the project are all involved in educational outreach as well. One of several examples was a Crystals and Clinker Teacher Workshop hosted at Mines in Oct, 2023 that introduced 20 middle- and high-school teachers to materials science concepts and activities. We also write papers, present at conferences, etc.

Data Management and Open Access

All of the films grown at NREL and Mines and their associated data collected on our collection of high-throughput instruments are (semi)automatically included in the HTEM (high throughput experimental materials) database (htem.nrel.gov), and we periodically add our low-throughput experimental data to the same. Data, metadata, and python scripts associated with our computational studies go on GitHub, then MDF. We also have a complementary tutorial on GitBook that is gradually being polished.

Fig. 2. The entire team and additional collaborators met at Broadcom in Feb, 2024 for an all-hands meeting and tour.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Our industry partner on this GOALI project has been intimately involved from the start and hosted the entire team (and a few others) for an all-hands project meeting and tour in Feb, 2024 (Fig. 2). There is no direct pipeline from our discovery-focused project to a specific product line, but the concepts and findings of this project are of great interest to Broadcom and may help to inform future product enhancements.

Publications and References

1. K. Yazawa, P. Gorai, J.S. Mangum, G.L. Brennecka, and A. Zakutayev, Local Chemical Origin of Ferroelectric Behavior in Wurtzites, J. Mater. Chem. C **10**, 17557 (2022). DOI: 10.1039/d2tc02682a

2. K. Yazawa, A. Zakutayev, and G. Brennecka, *High-Speed and High-Power Ferroelectric Switching Current Measurement Instrument for Materials with Large Coercive Voltage and Remanent Polarization,* Sensors **22**, 9659 (2022). DOI: 10.3390/s22249659

3. K. Yazawa, J. Hayden, J-P. Maria, W. Zhu, S. Trolier-McKinstry, A. Zakutayev and G.L. Brennecka, *Anomalously Abrupt Switching of Wurtzite-structured Ferroelectrics: Simultaneous Non-linear Nucleation and Growth Model* Mater. Horiz. **10**, 2936-44 (2023). DOI: 10.1039/D3MH00365E

4. S.R.J. Likith, G.L. Brennecka, and C.V. Ciobanu, *Interlayer Registry Effects on the Electronic and Piezoelectric Properties of Transition Metal Dichalcogenide Bilayers*, J. Vac. Sci. Tech. A **42**, 032201 (2024). DOI: 10.1116/6.0003264

5. K. Yazawa, D. Drury, J. Hayden, J.-P. Maria, S. Trolier-McKinstry, A. Zakutayev, and G.L. Brennecka, *Polarity Effects on Wakeup Behavior of $Al_{0.94}B_{0.06}N$ Ferroelectrics*, J. Am. Ceram. Soc. **107**, 1523-32 (2024). DOI: 10.1111/jace.19382

6. C.-W. Lee, N. Ud Din, K. Yazawa, G.L. Brennecka, A. Zakutayev, and P. Gorai, *Emerging Materials and Design Principles for Wurtzite-type Ferroelectrics* Matter **7**, 1644-59 (2024). DOI: 10.1016/j.matt.2024.02.001

7. C.-W. Lee, K. Yazawa, A. Zakutayev, G.L. Brennecka, and P. Gorai, *Switching it up: New Mechanisms Revealed in Wurtzite-type Ferroelectrics* Sci. Adv. **10**, eadl0848 (2024). DOI: 10.1126/sciadv.adl0848

8. C.-W. Lee, N. Ud Din, G.L. Brennecka, and P. Gorai, *Defects and Oxygen Impurities in Ferroelectric Wurtzite $Al_{1-x}Sc_xN$ Alloys*, Appl. Phys. Lett. **in press** (2024).

9. K. Yazawa, C. Evans, E. Dickey, B. Tellekamp, G.L. Brennecka, and A. Zakutayev, *Low Leakage Ferroelectric Heteroepitaxial $Al_{0.7}Sc_{0.3}N$ Films on GaN*, **in review** (2024).

Grain Interface Functional Design to Create Damage Resistance in Polycrystalline Metallic Materials

Lead Investigator: Curt A. Bronkhorst, cbronkhorst@wisc.edu.
Participating Institutions: Univ. of Wisconsin – Madison, Iowa State Univ., Univ. of New Hampshire.
Website: Under construction.
Keywords: Grain boundary, ductile damage mitigation, polycrystalline metal, interface, internal stress.

Project Scope

In high-purity tantalum, pores form at grain boundaries which are hypothesized to have a critical combination of high tensile stress and low tensile strength depending upon grain boundary type. Advanced single crystal theory will be developed to compute polycrystal internal stress state by coupling to an advanced macroscale ductile damage model. Grain boundary strength will be quantified via nanomechanical experiments and classical MD bicrystal calculations. Information theory and uncertainty quantification tools will be developed to integrate experimental and computed data to prescribe probable metal forming pathways to reduce porosity by 30% in a high triaxiality sample.

Relevance to MGI

The workflow for our *accelerated material design cycle to develop advanced damage resistant material* is shown in Figure 1. *Task 1* includes material processing and sample production for grain interface functional design encompassing advanced multi-level experiment with a focus on single/polycrystal characterization and grain boundary/interface interrogation. Task 1 will receive processing recipes from Task 3 and numerical simulations from Task 2. *Task 2* includes multi-level physical theory and code development along with numerical simulations. Task 2 will receive physical data from Task 1 and uncertainty quantification from Task 3. *Task 3* provides the statistical and uncertainty framework to enable rapid integration of experimental and computational data sets and statistical model development. Task 3 will receive computational results from Task 2 and experimental results from Task 1. Throughout this iterative process, improvements to all aspects of each task will be pursued. Our *measure of success* is to design and produce grain interface functionally designed polycrystalline Ta demonstrating *30% reduction in porosity* at equal deformation for the proposed multi-level, high-triaxiality sample in comparison to this projects reference rod and plate materials. Information integration of both advanced experimental and advanced physics-based computational origin will be critical to accelerated design.

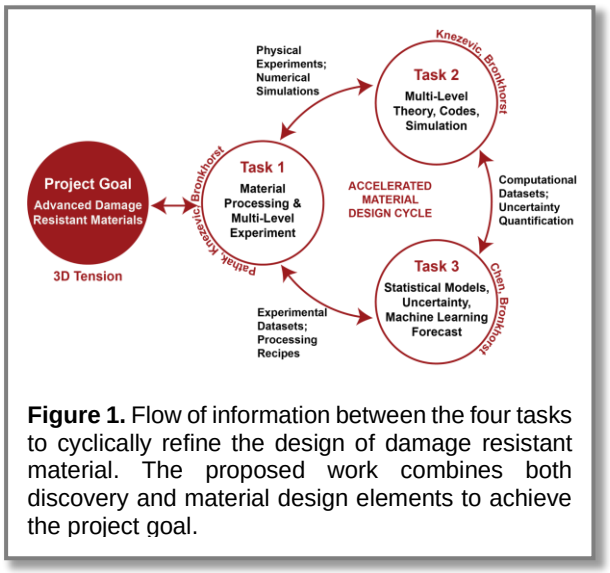


Figure 1. Flow of information between the four tasks to cyclically refine the design of damage resistant material. The proposed work combines both discovery and material design elements to achieve the project goal.

Technical Progress

Our work directly follows the hypothesis that spatial distribution of stress state and material defect weak spots combine to determine where and when pores form. We have been working to quantify both physical attributes of high-purity tantalum. Due to elastic and plastic anisotropy of metallic single crystals, polycrystal metals display significant intergranular interaction during deformation. The result of this interaction during deformation is significant variation on stress conditions with position in the material. Locations where stress is high contributes to higher probability for pore formation. It is not possible to experimentally measure local stress conditions in deformed materials, so we are using a soft-scale multi-scale modeling approach where we use an elastic-plastic-damage model to simulate specific experiments. An advanced crystal mechanics model for tantalum is being used to produce multi-scale simulation datasets. We have developed an information theory methodology which is able to use these physics computational datasets and attribute physical features and state of the material to high stress

spots located adjacent to grain boundaries and attribute their location to characteristics of the grains on each side of the boundary and their relative deformation behavior. The failure strength of grain boundaries is also being quantified. This physics dataset is based upon classical molecular dynamics (MD) bi-crystal calculations of varying grain boundary types. This computed dataset contains values of stress at which grain boundaries fail as a function of grain boundary type. The computed dataset provides quantitative grain boundary strength information but also provides physical insight into the process of grain boundary failure. Nano-indentation experiments are being performed in the vicinity of a collection of grain boundaries spanning a range of characters to provide supporting insight to assist in validating the MD dataset. These experiments include quantifying the indentation behavior of single crystals for a range of crystallographic orientation. MD simulations for the specific grain boundaries probed in the experiments will be conducted to provide direct parallels between experimental and simulation results.

Future Plans

The computed and experimental grain boundary datasets will be examined with our information theory methodology to attribute the observations to physical features of the boundaries. Micro-tension experiments will also begin to probe the tensile strength of grain boundaries and validate physical trends observed via bicrystal MD simulations. MD simulations will continue for the life of the project to add computed results to this grain boundary tensile strength dataset. Statistical model development will continue with emphasis to efficiently represent the probability density function evolutions of internal stress state and grain boundary strength with deformation. This will continue by introducing grain boundary misorientation into the computed and experimental datasets as a potentially important variable for microstructure design. A macroscale porosity-based ductile damage model will be developed for low deformation rate loading and will be used to simulate macroscale experiments, including the targeted high-triaxiality tension sample. This model is being developed with a new statistically based pore nucleation model based upon work of this project. This model will also be used to provide evolving stress conditions for micromechanical study at locations in the samples where damage probability is high. Our single crystal theories being used to produce our computational datasets have been improved for physical accuracy. We will begin performing quasi-static tension experiments on our target high-triaxiality tension sample together with forward calculations using crystal mechanics and the developed porosity-based ductile damage model.

Broader Impacts and Workforce Development

The educational impact of this work will be integrated across the three associated institutions by organizing targeted student exchanges among the PIs. The PI and three co-PIs will sponsor guest lecturing rotations within the courses they teach, as a cross-disciplinary effort, the shared and complementary expertise will be brought to the classroom. Graduate students from each research group will spend time between the three different institutions as part of each of the Ph.D. programs as well as possible internships at AFRL. Additionally, the UG capstone senior design courses at each department would particularly benefit from this arrangement, where the students will be mentored by experts from modeling, mathematics and experiments. The PIs are eager to build a very strong long-term collaborative relationship with AFRL and have existing collaborations with multiple U.S. National Laboratories to provide the students in the team with direct access to state-of-the-art user facilities, including their world class training on safety and research, and world-class staff. The PIs plan to provide a multitude of research opportunities *for upper level undergraduate students* (~8 students/year) via direct funding.

Data Management and Open Access

Once available, all results will be archived to a project identified repository on the UW Libraries MINDS@UW system which provides long-term preservation and open access to digital materials. This project will follow the best practice protocols established for the MINDS@UW system which adhere to FAIR data management and stewardship principles. The project website will direct the community to locations of all data and code.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The material production processes targeted in this project are generally available commercially and therefore the emphasis will be upon building the material design framework and methodology to enable more rapid manufacturing process design. The tools developed in this project are envisioned to be adapted in time to any material system or manufacturing process where both computational and experimental datasets are together used to determine high probability of success manufacturing procedures.

Publications and References

Najmabad, S. I., Olanrewaju, O. F., Pathak, S., Bronkhorst, C. A., Knezevic, M., *Crystal Plasticity Finite Element Simulations of Nanoindentation and Simple Tension for Yielding of Ta Crystals*. Int. J. Sol. Struct. 300, 112928 (2024). https://doi.org/10.1016/j.ijsolstr.2024.112928.

Zhang, Y., Chen, N., Bronkhorst, C. A., Cho, H., Argus, R., *Data-Driven Statistical Reduced-Order Modeling and Quantification of Polycrystal Mechanics Leading to Porosity-Based Ductile Damage*. J. Mech. Phys. Solids 179, 105386 (2023). https://doi.org/10.1016/j.jmps.2023.105386.

Chen, N, and Zhang Y. *A causality-based learning approach for discovering the underlying dynamics of complex systems from partial observations with stochastic parameterization.* Physica D: Nonlinear Phenomena 449, 133743 (2023). https://doi.org/10.1016/j.physd.2023.133743

Lee, S., Cho, H., Bronkhorst, C. A., Clausen, B., Pokharel, R., Brown, D. W., Anghel, V., Gray III, G. T., *Deformation, Dislocation Evolution, and the Non-Schmid Effect in Body-Centered-Cubic Single- and Polycrystal Tantalum*, Int. J. Plasticity 163, 103529 (2023). https://doi.org/10.1016/j.ijplas.2023.103529.

Architecting DNA Nanodevices into Metamaterials, Transducing Materials, and Assembling Materials

Lead Investigator: Carlos Castro, castro.39@osu.edu
Participating Institutions: The Ohio State University, Duke University
Source of Support: NSF-DMREF
Website: none
Keywords: DNA nanotechnology, DNA origami, single molecule dynamics, biomolecular materials, self-assembly

Project Scope

This work is developing self-assembled materials constructed from DNA with adaptable structures and unique mechanical properties, signal processing capabilities, and variable material properties from a single reconfigurable building block. We will construct these materials from nanoscale DNA building blocks with precisely designed structure and tailored mechanical and dynamic properties guided by molecular modeling. These units will be constructed into assemblies consisting of many devices that interact with each other to coordinate functions including signal transduction, shape morphing, and polymorphic assembly. We will establish design principles for on-demand material properties using molecular simulation and machine learning approaches.

Relevance to MGI

This project integrates molecular modeling, DNA-based design, and single molecule characterization to develop self-assembling materials based on dynamic nanodevices, where properties and interactions of nanodevices drive emergent behaviors of the material (Figure 1). The design of DNA nanodevices is guided by integration of design, experiments, and molecular simulations used to predict properties such as motion or stiffness. These properties are characterized by single molecule methods, and experimental results are used to refine designs and modeling approaches, while models are then leveraged to guide design of assemblies. At the assembly scale, we closely couple experimental fabrication and characterization with a combination of coarse-grained molecular dynamics simulations, Brownian dynamics simulations, and theoretical modeling to achieve desired collective material behaviors (i.e. shape morphing and signal processing). We leverage opensource software tools for DNA origami (DO) design and have developed coarse grained models that advance the capabilities to predict behaviors of DNA based materials. Using these approaches, we are establishing assemblies with variable properties and signal transmission capabilities.

Technical Progress

To date we have made progress in four areas: 1) development of coarse-grained models for simulating assembly and dynamics of DO structures; 2) design and single molecule characterization of signal transmitting devices; 3) scalable and sustainable fabrication methods for DO devices; and 4) higher order self-assembly of reconfigurable DO building blocks.

We developed a coarse-grained model designed to simulate events like assembly and reconfiguration, which occur at timescales beyond what could previously be captured by other DO simulation approaches. Where previous approaches coarse grain at the level of bases or base-pairs (bp), our approach coarsens the DNA structure at the level of 8 bp units, a typical unit of continuous base-pairing in DO structures. We demonstrated this model can simulate self-assembly of a full size (~7,000 bp) DO, not possible with prior approaches. This work was recently published in *Nature Communications* [1].

In addition, we made significant progress with simulation guided design and single molecule characterization of signal transducing devices. We

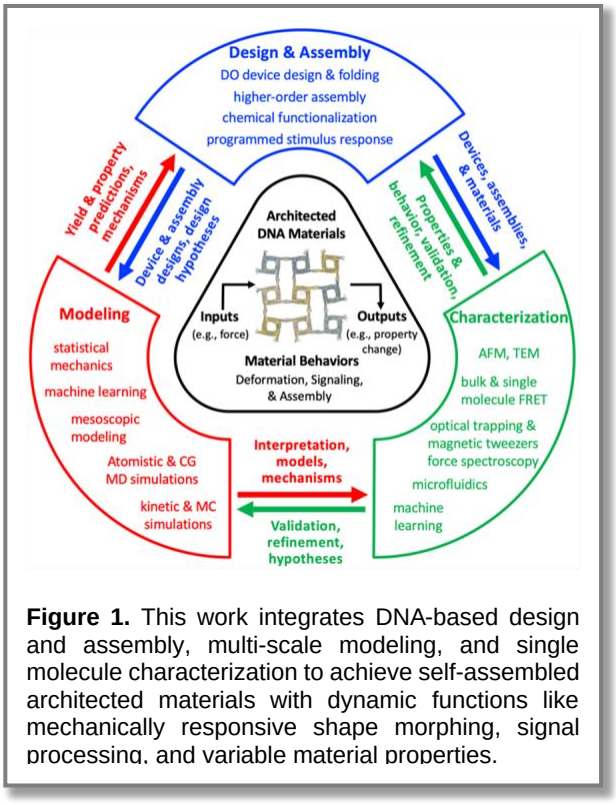


Figure 1. This work integrates DNA-based design and assembly, multi-scale modeling, and single molecule characterization to achieve self-assembled architected materials with dynamic functions like mechanically responsive shape morphing, signal processing, and variable material properties.

designed a switch-like device that exhibits two states: latched to the left or latched to the right. We developed single molecule assays to measure the transitions between these states, which show the device switches rapidly between the right latched and left latched state in about 100 milliseconds. Moving forward we will assemble these switching devices into assemblies that can transmit, transduce, and process signals.

We also developed approaches to improve efficiency of DO self-assembly by recycling the DNA components. Briefly, we developed two recycling methods. The first enables reprogramming of folded DO structures into brand new structures, allowing re-use of the template single-stranded DNA (ssDNA) scaffold. The second significantly improves sustainability and cost-effectiveness of DO fabrication, which is carried out with a large excess of ssDNA staple strands (~10 times excess) that fold the scaffold into the desired structure. Typically, the excess staples are wasted, but we established a method to recover these excess staple strands after folding and show these can be used to reliably fold new devices. This work is detailed in a preprint [2] and is currently under review for publication.

Finally, we made progress in developing reconfigurable DO devices that can self-assemble into a variety of different higher order assemblies depending on their configuration. These reconfigurable units can bind together in multiple orientations, which leads to either more or less compact microstructure in higher order assemblies.

Future Plans

In addition to publishing key studies, we will build off our work on single signal transducing devices to develop filaments and networks of polymerized signal transducing devices for long range signal transduction. A key focus will be on determining the time scale and fidelity of the communication. We have demonstrated local plasmonic heating with gold nanoparticles, which we will integrate for triggering. Separately, we will investigate the time scale of self-assembly of DOs based on triggered reconfiguration of the DOs. Now that we have constructed single reconfigurable DOs that also self-assemble into networks, we will investigate the time scale for trigger reconfiguration of DO networks and how an external force influences the reconfigurations. We will also continue the development of Langevin coarse-grained models to understand the kinetics of single DO devices and network assemblies, which provide key mechanistic insight into DO performance and design optimization.

Broader Impacts and Workforce Development

We have continued to support design and simulation workshops with lab members and with undergraduate students to train users on our previously developed software tool MagicDNA. We manage a Slack channel where users can get support on design software (available on github). We also again ran a two-week Summer workshop where ~30 first year students at OSU learned to design DO and run simulations using online tools. Finally, building on prior work where we developed experiment modules that can be carried out in elementary, high school, or undergraduate classrooms [5], we are now developing a similar module focused on DO higher order assembly.

Data Management and Open Access

Use of our previously developed design software MagicDNA is supported with workshops and tutorials on youtube (https://www.youtube.com/channel/UCpI3shjsdy89Xg2iVt-ZYCw). We manage communication among our team and with users through Slack and share documents, data, and protocols over Teams. Several of our published DO designs are uploaded to the DNA nanostructure design repository (e.g., https://nanobase.org). And we have consistently shared work via preprints at the time of submission for peer-reviewed publication.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We are developing materials well-suited for applications in biosensing, nanocomputing, nanomanufacturing, and nanorobotics. The PI is working towards translation of a biosensor device that is based on earlier NSF-supported developments. The work in progress through this grant can provide a number of key advancements in the areas of multiplexing, intelligent detection (i.e. signal processing), mechanical sensing, new detection readouts, and signal amplification.

Publications and References

1. DeLuca, M., D. Duke, T. Ye, M. Poirier, Y. Ke, C. Castro, and G. Arya, *Mechanism of DNA origami folding elucidated by mesoscopic simulations.* Nature Communications, 2024. **15**(1): p. 3015.
2. Neuhoff, M.J., Y. Wang, N.J. Vantangoli, M.G. Poirier, C.E. Castro, and W.G. Pfeifer, *Recycling Materials for Sustainable DNA Origami Manufacturing.* bioRxiv, 2024: p. 2024.06.05.596853.

Multi-material digital light processing of functional polymers

Lead Investigator: Michael Chabinyc,[1] Christopher Bates,[1] Angela Pitenis,[1] Adarah Krishnamurthy,[2] Soumik Sarkar,[2] Baskar Ganapathysubramanian[2]
Participating Institutions: [1]University of California Santa Barbara, [2]Iowa State University
Source of Support: NSF-DMREF
Website: https://dmref.org/projects/348
Keywords: polymers, additive manufacturing, digital twin, digital light processing

Project Scope

Digital light processing (DLP) is a powerful additive manufacturing method for soft materials. DLP exploits control over light irradiation to solidify a resin defining the shape of printed parts. Current DLP techniques are restricted in their ability to print multiple materials with different properties (e.g. to vary elasticity) in a single exposure step. Our project aims to: (1) Design multi-material DLP resins that orthogonally cure to yield materials with extreme contrast in mechanical properties, (2) Develop digital twins of multi-material DLP that leverage machine learning (ML) surrogate models for inverse design of DLP for multi-material structures, and (3) Design multi-material structures to direct cell behavior with varying stiffness that is topology optimized (Figure 1).

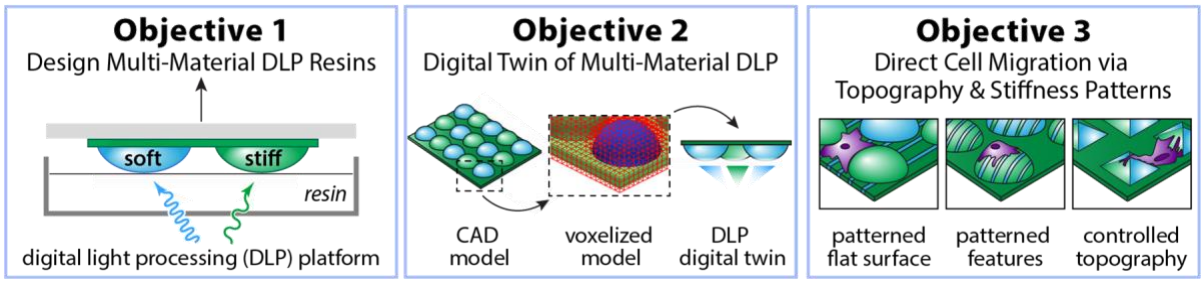


Figure 1. Overview of the project to achieve multi-material structures that can direct the behavior of biological cells.

Relevance to MGI

The challenges associated with multi-material DLP cut across scientific disciplines and require the closed-loop approach of the MGI. While the physical behavior of polymer networks can be informed by existing theory, there is no efficient way to optimize the complex formulations used in multi-material resins. To address these challenges, we propose to use machine learning, which will accelerate the discovery of fundamental chemistries and help translate them into practice. The need to optimize the coupled and controllable interactions between light, chemistry, and mechanics serves as an ideal multi-physics testbed to build and deploy the next generation of scientific machine learning (SciML) approaches for multi-physics simulations. We will leverage our prior experience to create datasets and models from our high-throughput experimentation, simulations, and artificial intelligence to strengthen the ties between materials chemistry and data science. Exploiting this convergent approach spanning materials synthesis, characterization, scientific computing, and data science to workforce training for graduate students who communicate across the traditional research divide provides an important foundation for future industries.

Technical Progress

The development of multi-material resins with extreme contrast in mechanical properties requires definition of chemistries that achieve supersoft properties as well as conventional stiff networks. We have initially focused on the development of supersoft polymer networks using materials chemistries based on a slide ring architecture. Slide ring networks offer unique opportunities for control of mechanical modulus and toughness based on their composition because of the dynamics of the network.

Our initial work shows that networks formed using cyclodextrin-based rings and poly(ethylene glycol) threads to crosslink polyacrylamide chains lead to soft, tough gels with exceptionally low friction coefficients. The slide-ring gels had low reduced moduli, $E^* < 20$ kPa, relative to comparable conventional networks, $E^* \approx 100$ kPa while still maintaining good mechanical toughness. Analysis of the dependence of the friction coefficient upon loading

revealed that the slide ring gels provided thicker fluid lubrication layers at their surface leading to very low friction coefficients ($\mu < 0.01$). These observations suggest that the slide ring architecture is suitable for forming multi-material structures with high contrast between mechanical properties.

Figure 2. Creating interlocked multi-material parts. The black (gray) material is hard while the red material is soft. We algorithmically generate interlocking 3D pegs at the interface. (Left) CAD models of the 2 materials with interlocking pegs; (Middle) slice of the multi-material part; (Right) picture of a slice of the actual part.

In parallel, we are developing computer-aided design (CAD) tools to create physically interlocked parts (Figure 2). We modify the joint region between the hard and soft materials so that they do not separate during operation. We have developed an algorithm that will create tiles of interlocking 3D pegs at the intersecting region. These pegs physically interlock the hard and soft parts. Generating the CAD models for multi-material parts will be the first step in creating a multiscale digital twin of the 3D printing process. We have also been working on developing a computational framework to model the light transport inside the resins to as part of a digital twin will enable us to predict the material properties of parts with complex geometry based on the light exposure time.

Future Plans

Our near-term goal is to develop a workflow for optimization of the mechanical properties of slide ring gels based on the formulation of the multi-component resin. We will leverage a robotic system for high throughput mixing of varying formulations along with a high throughput mechanical tester for cured resins to generate a training data set for AI/ML methods. We will make use of Reinforcement Learning (RL) to identify the most promising formulations for the next campaign of the gels based on the results of the mechanical tester. We will develop suitable reward functions that will provide control of the required mechanical properties. Once we have defined appropriate resin compositions to achieve desirable mechanical properties, we will further modify the resins for 3D printing conditions. A computational framework for a digital twin of the light-based 3D printing process that incorporates light exposure and chemical kinetics is under development.

Broader Impacts and Workforce Development

The PIs endeavor to involve a diverse cohort of graduate students in the project and they mentor a significant number of diverse undergraduate researchers. The PIs are developing new modules for teachers from 6^{th} to 8^{th} -grade levels that emphasize "Developing and Using Models" – a key concept in the Next Generation Science Standards for California Public Schools. We are leveraging the new Student Innovation Center (SICTR) and the Translational AI Center (TrAC) at ISU to enable tech transfer of the innovative technologies developed as part of this project. We have also been offering introductory AI courses as part of the new microcredentials initiative at ISU.

Data Management and Open Access

The variety of instrumentation used in the project along with the computational models will generate diverse data types, particularly for high throughput experiments. We will adhere to FAIR methods and properly link experimental data with metadata and use the DRYAD site for archiving data with DOIs.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Our research to accelerate the design of materials and methods for 3D printing demonstrates a platform for a tight feedback loop between experiments and machine learning to develop new artificial intelligence and big data methods that provide insights into (i) novel structure--property relationships and (ii) optimal processing strategies that leverage enabling chemistry and inverse design. We anticipate that multi-material resins and the methodologies for optimization will be of interest to industries developing next generation soft materials for applications in biomedicine and soft robotics.

Publications and References

1. I. Lapkriengkri, K. R. Albanese, A. Rhode, A. Cunniff, A. A. Pitenis, M. L. Chabinyc, C. M. Bates *Chemical Botany: Bottlebrush Polymers in Materials Science* Ann. Rev. Mater. Sci. **54** 3.1-3.20 (2024) https://doi.org/10.1146/annurev-matsci-091522- 024148

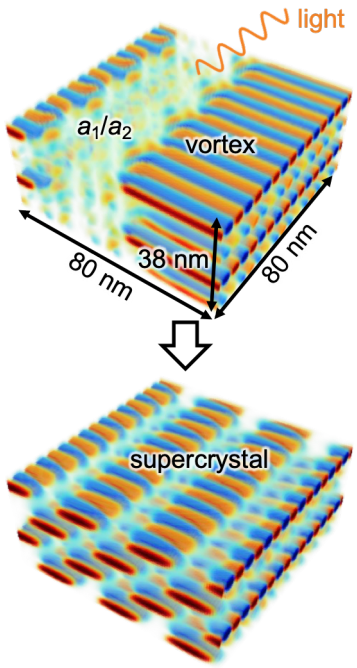
2. A. R. Rhode, I. Montes de Oca Estrada, M. L. Chabinyc, C. M. Bates, A. A. Pitenis *Sliding on Slide-Ring Gels* Tribol. Lett. submitted (2024).

Thermodynamics and Phase-field Simulations of Light-induced Transformations of Mesoscale Polar Structures

Lead Investigator: Long-Qing Chen, lqc3@psu.edu
Participating Institutions: Penn State University, Univ of Wisconsin Madison, and Ukraine Academy of Sciences
Source of Support: DOE-BES-CMS
Website: https://sites.psu.edu/doecomms/
Keywords: mesoscale, phase-field, phase transitions, ferroelectrics, domain patterns

Project Scope

The main objective of this research is to understand the light-induced mesoscale phase transformations of polar structures by developing and using a phase-field model that explicitly incorporate both structural and electronic processes. Employing a $PbTiO_3/SrTiO_3$ ferroelectric superlattice as an example, we demonstrate that the light-excited carriers provide the charge compensation of polarization bound charges and the lattice thermal energy, both of which are key to the thermodynamic stabilization of a previously observed supercrystal, a three-dimensionally periodic nanostructure, within a window of substrate strains, while different mechanical and electrical boundary conditions can stabilize a number of other nanoscale polar structures by balancing the competing short-range exchange interactions responsible for the domain wall energy and long-range electrostatic and elastic interactions. The insights on the light-induced formation and richness of nanoscale structures from this work offer theoretical guidance for exploring and manipulating the thermodynamic stability of nanoscale polar structures employing a combination of thermal, mechanical, and electrical stimuli as well as light.



The $PbTiO_3/SrTiO_3$ superlattice transforms from a pristine state consisting of vortex tube and a_1/a_2 twin domain regions to a 3-dimensional ferroelectric supercrystal upon application of an above-bandgap light pulse.

Relevance to MGI

This work involves close collaborations with several experimental groups including both the in-house experiments by co-PI Gopalan and extensive external collaborations. Specifically, we heavily leverage unique facilities through other DOE projects (DE-SC0012375, "*Ultrafast Creation of Emergent Phenomena and Metastable Phases in Complex Oxides*," and the LCLS Campaign grant (LW00) titled "*Fluctuations, Emergence, and Dynamics of Complex Topological Supertextures by Design*." The two projects involve the extensive use of X-ray free electron lasers at Linac Coherent Light Source (LCLS, Stanford), Advanced Photon Source (Argonne, IL), and ultrafast and nonlinear optical characterization at Penn State and other places.

Technical Progress

We have developed a dynamical phase-field model (DPFM) for modeling the co-evolution of electronic carriers and ferroelectric domains and the accompanying mesoscale pattern evolution under static or ultrafast external stimuli [1]. As an illustrative example of application, we study the transient dynamic response of ferroelectric domain walls excited by an ultrafast above-bandgap light pulse. We discover a two-stage relaxational electronic carrier evolution and a structural evolution containing multiple oscillational and relaxational components across

picosecond to nanosecond timescales. The phase-field model offers a general theoretical framework which can be applied to a wide range of functional and quantum materials with interactive electronic and lattice orders and phase transitions to understand, predict, and manipulate their ultrafast dynamics and rich mesoscale evolution dynamics of domains, domain walls, and charges.

Our phase-field simulations using the dynamic phase-field model reveal the existence of rich mesoscale structures that can transform from one to another under external biases and the key role of electronic charge carriers in the thermodynamic stability and phase transitions among different mesoscale polar phases induced by an above-bandgap excitation [2]. In particular, we identify the key thermodynamic driving forces for the emergence of the ferroelectric supercrystal, including electrostatic charge compensation and supply of thermal energy by the light-excited charger carriers as well as an appropriate range of substrate mechanical constraints. We further discover the thermodynamic stability of several additional nanoscale ferroelectric domain structures upon optical excitations under different substrate strains and electric field biases. The findings provide theoretical insights into the mesoscale thermodynamics of light-induced structural transitions in ferroelectric superlattices, which are expected to stimulate future experiments on the formation and properties of novel polar states.

Our phase-field simulations provided guidance to understanding experimentally observed light-induced mesoscale polar structures by collaborators. For example, the dynamic phase-field simulations guided the understanding of the experimentally observed pathways by single-shot optical-pump, X-ray-probe measurements from an initially heterogenous mixture of polar phases going through a transient mixture of disordered ferroelectric and suppressed vortex orders, then, labyrinthine fluctuations accompanied by the reemergence of vortex order, and to the eventual emergence of a single vortex supercrystal phase [3]. Our phase-field simulations also elucidated the underlying mechanisms through the interplay between photocarriers and transient lattice temperature for the reconfiguration of the polar domain networks. The simulations help understand the evolution of nanodomain networks in $(PbTiO_3)_n/(SrTiO_3)_n$ superlattices directly visualized in real space as the system adapts stage-by-stage to tailored ultrafast repetitive optical excitations [4].

Future Plans

We plan to develop a GPU-accelerated finite-difference method-based 3D dynamical phase-field model that incorporates coupled dynamics of strain, polarization, charge, and electromagnetic waves in ferroelectrics-based multiphase system and the corresponding software module, Q-Pop-FerroDyn, to simulate the nonlinear interaction between strong transient THz/optical pulse and ferroelectric systems with inhomogeneous polarization patterns. We will demonstrate the possibility of performing basic quantum operation (Rabi oscillation and Ramsey interference) for quantum computing based on strongly coupled THz photons and optical phonons (polarization). We also plan to develop a new characterization tool (Q-POP-NLO) for the direct evaluation of second-harmonic generation (SHG) and other non-linear optical responses in ferroelectric crystals with arbitrary polarization distributions.

Publications and References

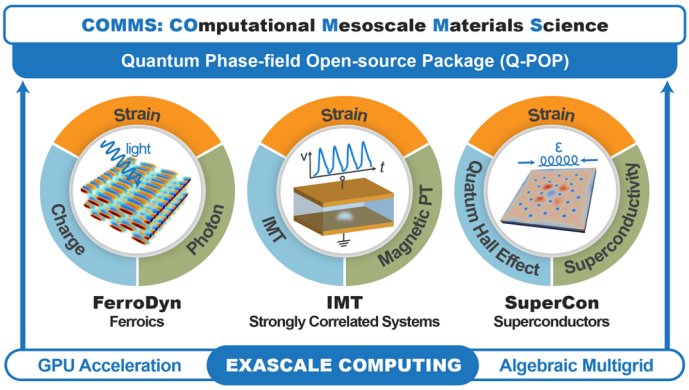
1. T.N. Yang and L.Q. Chen, *Dynamical phase-field model of coupled electronic and structural processes*. npj Computational Materials **8**(1),130 (2022), 10.1038/s41524-022-00820-9.
2. T.N. Yang, C. Dai, and L.Q. Chen, T*hermodynamics of Light-Induced Nanoscale Polar Structures in Ferroelectric Superlattices*. Nano Letters, **23**(7): p. 2551-2556 (2023): 10.1021/acs.nanolett.2c04586.
3. V.A. Stoica, T. Yang, S.D. Das, Y.C. Cao, H. Wang, Y. Kubota, C. Dai, H. Padmanabhan, Y. Sato, A. Mangu, Q.L. Nguyen, Z. Zhang, D. Talreja, M.E. Zajac, D.A. Walko, A.D. DiChiara, S. Owada, K. Miyanishi, K. Tamasaku, T. Sato, J.M. Glownia, V. Esposito, S. Nelson, M.C. Hoffman, R.D. R.D. Schaller, A.M. Lindenberg, L.W. Martin, R. Ramesh, I. Matsuda, D. Zhu, L.Q. Chen, H. Wen, V. Gopalan, and J.W. Freeland, *Non-Equilibrium Pathways to Form Emergent Polar Supertextures.* Nature Materials, 2024. Accepted
4. M. Zajac, T. Zhou, T. Yang, S. Das, Y. Cao, B. Guzelturk, V. Stoica, M. Cherukara, J.W. Freeland, V. Gopalan, R. Ramesh, L.W. Martin, L.Q. Chen, M. Holt, S. Hruszkewycz, and H. Wen, *Optical Control of Adaptive Nanoscale Domain Networks.* Advanced Materials, 2024. Accepted.

COMMS: Computational Mesoscale Materials Science

Lead Investigator: L.Q. Chen[1] (lqc3@psu.edu); Co-PI's: Dabo[1], Eliseev[2], Gopalan[1], Hao[1], Hu[3], Morozovska[2]
Participating Institutions: [1]Penn State University, [2]Ukraine Academy of Sciences, [3]Univ of Wisconsin at Madison
Source of Support: DOE-BES-CMS
Website: https://sites.psu.edu/doecomms/
Keywords: mesoscale, phase-field, phase transitions, quantum materials, domain patterns

Project Scope

The goal of COMMS is to develop mesoscale models, numerical algorithms, and software for quantum and functional materials. The specific efforts are to: (1) Further extend our dynamic phase-field model of coupled structural and electronic carrier dynamics to photon dynamics; (2) Construct a set of novel phase-field models of coupled electronic and structural phase transitions; (3) Develop and deploy the corresponding software modules; and (4) Experimentally validate and refine the theory and computational tools through extensive collaborations with experts outside the core team. An outcome is a software, Q-POP, for understanding microstructures of quantum and functional materials.



Thrust 1: Coupled polarization, photon and elastodynamics with charge
Thrust 2: Coupled insulator-metal and magnetic transitions with strain
Thrust 3: Coupled superconducting and strain or quantum hall effect

Relevance to MGI

This DOE Computational Materials Science Project involves close collaborations with many experimental groups including both the in-house experiments by co-PI Gopalan and extensive external collaborations. Specifically, we heavily leverage **unique facilities** through other DOE projects (DE-SC0012375, "*Ultrafast Creation of Emergent Phenomena and Metastable Phases in Complex Oxides*," and the LCLS Campaign grant (LW00) titled "*Fluctuations, Emergence, and Dynamics of Complex Topological Supertextures by Design*." The two projects involve the extensive use of X-ray free electron lasers at Linac Coherent Light Source (LCLS, Stanford), Advanced Photon Source (Argonne, IL), and ultrafast and nonlinear optical characterization at Penn State and other places. The team also leverages existing collaborations, through funded projects and beamline proposals, with about a dozen experimental groups such as D. G. Schlom (PARADIM, Cornell, MBE Growth), R. Engel-Herbert (Paul Drude Institute for Solid State Electronics (Berlin, Germany)), L. Martin (Rice, multiferroic oxide heterostructures), J. Chakhalian (Rutgers, laser MBE of nickelate thin films), Z. Mao (Penn State, single crystal growth of ruthenates and other oxide), A. Lindenberg (Stanford/SLAC, X-ray and electron scattering and spectroscopic techniques and ultrafast optical techniques), J. Freeland and H. Wen (Advanced Photon Source at the Argonne National Labs, time-resolved ultrafast X-ray diffraction and microscopy, magnetic scattering), X. Zhang (Northeastern, ferroic and quantum devices).

Technical Progress

Insulator-to-metal (IMT) Transitions in the Strongly Correlated VO_2: Our team not only pioneered the phase-field model development of metal-insulator transitions but also using the example of VO_2 to reveal a fascinating electro-chemo-mechanical mechanism at play that includes coupled electronic-structural phase transitions in the presence of oxygen vacancies, the simultaneous evolution dynamics of electronic carriers, structural orders, as well as new non-equilibrium phases [1]. This teamwork has also led to the computational prediction of intrinsic self-oscillations [2] and the discovery that the vacancy redox reactions and the insulator-metal transitions mutually promote each other, leading to faster voltage self-oscillations in VO_2 [3].

Discovery of Sublattice-Dependent Antiferromagnetic Transition in Perovskite Nickelates [4]: We used the Landau theory to investigate the coupled insulator-metal, structural, and magnetic phase transitions in another fascinating correlated material, perovskite rare earth nickelates. We reproduced the experimentally measured temperature-tolerance factor phase diagram and found that the antiferromagnetic transition is sublattice-dependent, which illustrates the existing but confusing experimental susceptibilities. Our results also proved the noncollinear nature of the magnetic structure of bulk nickelates, shedding new light on the relevant long-standing debate.

Coupled Electron and Lattice Systems in Correlated Material Systems: We have established a novel dynamical phase-field model for coupled electron and lattice systems in strongly correlated materials under ultrafast excitation on the ps-ns timescales and model the electronic and lattice dynamic responses of the non-equilibrium states of the prototypical correlated material $Ca_3Ru_2O_7$ on the ultrafast timescales [5]. We also formulated a comprehensive mesoscale thermodynamic model of coupled electronic phase transitions including metal-insulator transitions, magnetic phase transitions, charge density waves (CDW) formation, superconducting phase transitions [6].

Mesoscale Modeling of Complex Topological Polar Structures: We have developed a *dynamical* phase-field model (DPFM) for modeling the co-evolution of electronic carriers and ferroelectric domains [7]. Our phase-field simulations reveal the existence of rich mesoscale structures that can transform from one to another under external biases and the key role of electronic charge carriers in the thermodynamic stability and phase transitions among different mesoscale polar phases induced by an above-bandgap excitation [8]. In particular, we demonstrate that the light-excited carriers provide the charge compensation of polarization bound charges and the lattice thermal energy, both of which are key to the thermodynamic stabilization of a previously observed supercrystal, a three dimensionally periodic nanostructure.

Numerical Algorithm and Open-Source Software Package Developments: Our team has made substantial progress in enhancing solvers for phase-field equations, achieving significant improvements in speed and made significant progress on the Q-POP framework, an open-source suite designed for flexible phase-field simulations. The initial release offers a variety of capabilities, including modules for simulating insulator-metal transitions (Q-POP-IMT) with documentation. Furthermore, we have developed several pre- and post-simulation utility tools including a routine (Q-POP-Diffraction) to compute the X-ray diffraction patterns of phase-field predicted structures to allow a direct comparison between phase-field simulations and diffraction experiments [11]. We have developed a software tool to simulate the second harmonic generation (SHG) termed ♯SHAARP of crystals [12].

Future Plans

Develop the macroscopic superconducting phase-field model in entire-temperature regime by extracting dynamics from microscopic superconducting theory; incorporate the coupling of the superconducting order parameter with other quantum orders and fluctuations and calculate the temperature-doping/density phase diagram of the fluctuating and high-T_c superconductivity; and develop the phase-field model of the superconducting phase coherence in Josephson junctions, and design/propose the scheme for experimental quantum devices.

Develop a new characterization tool (Q-POP-NLO) for the direct evaluation of second-harmonic generation (SHG) and other non-linear optical responses in ferroelectric crystals with arbitrary polarization distributions and a GPU-accelerated finite-difference method based 3D dynamical phase-field model that incorporates coupled dynamics of strain, polarization, charge, and electromagnetic waves in ferroelectrics-based multiphase system (Q-Pop-FerroDyn) to simulate the nonlinear interaction between strong transient THz/optical pulse and ferroelectric systems with inhomogeneous polarization patterns; and demonstrate the possibility of performing basic quantum operation (Rabi oscillation and Ramsey interference) for quantum computing based on strongly coupled THz photons and optical phonons (polarization).

Develop robust and efficient solvers for Maxwell's equations in mixed formulation, ensuring the parameter robustness and design advanced time discretization methods and corresponding fast solvers for the time-dependent Ginzburg-Landau model to significantly enhance simulation efficiency; Develop fast and robust solvers specifically for phase-field models that are coupled with Maxwell's equations in mixed formulation.

Advance the implementation of highly-performant, portable, and scalable multigrid, finite-element solvers for phase-field equations governing insulator-metal transitions, electron carrier dynamics, polarization dynamics, spin dynamics, and superconducting phase transitions. To achieve this, exascale-capable libraries such as FEniCS-DOLFINx (CPUs-only) and MFEM (supporting both CPU and GPU architectures) will be leveraged.

Publications and References

1. G. Stone, Y. Shi, M. Jerry, V. Stoica, H. Paik, Z. Cai, D. G. Schlom, R. Engel-Herbert, S. Datta, H. Wen, L.-Q. Chen, V. Gopalan, *In-Operando Spatiotemporal Imaging of Coupled Film-Substrate Elastodynamics During an Insulator-to-Metal Transition*. *Advanced Materials* 2312673 (2024)
2. Y. Shi and L.Q. Chen, *Intrinsic Insulator-Metal Phase Oscillations*. Physical Review Applied **17**(1): 014042 (2022), 10.1103/PhysRevApplied.17.014042.
3. Y. Shi, V. Gopalan, and L.Q. Chen, *Phase-field model of coupled insulator-metal transitions and oxygen vacancy redox reactions*. Physical Review B **107**(20): L201110 (2023), 10.1103/PhysRevB.107.L201110.
4. Y. Shi and L.Q. Chen, *Sublattice-Dependent Antiferromagnetic Transitions in Rare Earth Nickelates*. Physical Review Letters **130**(18): 186801 (2023), 10.1103/PhysRevLett.130.186801.
5. T.N. Yang, Y. Xiong, Y. Wang, Y. Shi, V. Gopalan, I. Dabo, and L.Q. Chen, *Phase-field model of electron and lattice dynamics in correlated material systems*. Physical Review Letters, 2023. Under revision
6. 1. A. Morozovska, E. Eliseev, V.Gopalan and L.-Q. Chen. *Landau-Ginzburg theory of charge density wave formation accompanying lattice and electronic long-range ordering*. Physical Review B **107**, 174104 (2023), https://link.aps.org/doi/10.1103/PhysRevB.107.174104
7. T.N. Yang and L.Q. Chen, *Dynamical phase-field model of coupled electronic and structural processes*. npj Computational Materials **8**(1),130 (2022), 10.1038/s41524-022-00820-9.
8. T.N. Yang, C. Dai, and L.Q. Chen, T*hermodynamics of Light-Induced Nanoscale Polar Structures in Ferroelectric Superlattices*. Nano Letters, **23**(7): p. 2551-2556 (2023): 10.1021/acs.nanolett.2c04586.
9. Q.G. Hong, L.M. Ma, J.C. Xu, and L.Q. Chen, *An efficient iterative method for dynamical Ginzburg-Landau equations*. Journal of Computational Physics **474**, 111794 (2023), 10.1016/j.jcp.2022.111794.
10. Q. Hong, L. Ma, D. Fortino, L. Q. Chen, and J. Xu. *An Efficient Numerical Algorithm for Solving Coupled Time-Dependent Ginzburg-Landau Equation for Superconductivity and Elasticity*. Communications in Computational Physics. Accepted, (2024).
11. T.N. Yang, C. Dai, V.A. Stoica, F. Xue, H.Y. Wang, Y.Z. Ji, V. Gopalan, and L.Q. Chen, *Computing diffraction patterns of microstructures from phase-field simulations.* Acta Materialia, 2022. **239**: 118258, 10.1016/j.actamat.2022.118258.
12. R. Zu, B. Wang, J.Y. He, J.J. Wang, L. Weber, L.Q. Chen, and V. Gopalan, *Analytical and numerical modeling of optical second harmonic generation in anisotropic crystals using #SHAARP package*. npj Computational Materials **8**(1): 246 (2022), 10.1038/s41524-022-00930-4.
13. Y. Wang, Y.H. Xiong, T.N. Yang, Y.K. Yuan, S.L. Shang, Z.K. Liu, V. Gopalan, I. Dabo, and L.Q. Chen, *Thermodynamic and electron transport properties of $Ca_3Ru_2O_7$ from first-principles phonon calculations and Boltzmann transport theory*. Physical Review B **107**(3), 035118 (2023), 10.1103/PhysRevB.107.035118.
14. Y. Shi, J. Schirmer, and L.-Q. Chen, *Hall coefficient and resistivity in the doped bilayer Hubbard model*. Physical Review B 109 (7), 075114 (2024).
15. E. A. Eliseev, A. N. Morozovska, Y. M. Vysochanskii, L. P. Yurchenko, V. Gopalan and L.-Q. Chen. *Light-Induced Transitions of Polar State and Domain Morphology in Photo-Ferroelectric Nanoparticles*. Physical Review B **109,** 045434 (2024), https://doi.org/10.1103/PhysRevB.109.045434
16. Y. Shi, G.D. Zhao, I. Dabo, S. Ramanathan, and L.Q. Chen, *Phase-Field Model of Electronic Antidoping.* Phys. Rev. Lett. **132**, 256502 (2024), 10.1103/PhysRevLett.132.256502.
17. M. Zajac, T. Zhou, T. Yang, S. Das, Y. Cao, B. Guzelturk, V. Stoica, M. Cherukara, J.W. Freeland, V. Gopalan, R. Ramesh, L.W. Martin, L.Q. Chen, M. Holt, S. Hruszkewycz, and H. Wen, *Optical Control of Adaptive Nanoscale Domain Networks.* Advanced Materials, 2024. Accepted.
18. V.A. Stoica, T. Yang, S.D. Das, Y.C. Cao, H. Wang, Y. Kubota, C. Dai, H. Padmanabhan, Y. Sato, A. Mangu, Q.L. Nguyen, Z. Zhang, D. Talreja, M.E. Zajac, D.A. Walko, A.D. DiChiara, S. Owada, K. Miyanishi, K. Tamasaku, T. Sato, J.M. Glownia, V. Esposito, S. Nelson, M.C. Hoffman, R.D. R.D. Schaller, A.M. Lindenberg, L.W. Martin, R. Ramesh, I. Matsuda, D. Zhu, L.Q. Chen, H. Wen, V. Gopalan, and J.W. Freeland, *Non-Equilibrium Pathways to Form Emergent Polar Supertextures.* Nature Materials, 2024. Accepted
19. A. Mangu, V.A. Stoica, H. Zheng, T. Yang, M. Zhang, H. Wang, Q.L. Nguyen, S. Song, S. Das, P. Meisenheimer, E. Donoway, M. Chollet, Y. Sun, J.J. Turner, J.W. Freeland, H. Wen, L.W. Martin, L.Q. Chen, V. Gopalan, D. Zhu, Y. Cao, and A.M. Lindenberg, *Hidden Domain Boundary Dynamics Towards Crystalline Perfection.* Nature Physics, 2024. Submitted:
20. S. Hazra, T. Schweigert, A. Ross, H.D. Lu, U. Saha, V. Trinquet, A. Mangu, S. Sarkar, T. Kuznetsova, S. Sarker, M. Barone, R. Engel-Herbert, A. Lindenberg, G.-M. Rignanese, D.A. Muller, S. Salmanie-Rezzaie, V.A. Stoica, A. Gruverman, L.Q. Chen, D.G. Schlom, and V. Gopalan, *Giant Strain Tuning of Ferroelectricity in $KNbO_3$ Thin Films.* Advanced Materials, 2024. Submitted:

DMREF: GOALI: Designing Materials for Next-generation Spintronic Devices

Lead Investigator: Zhihong Chen, zhchen@purdue.edu
Participating Institutions: Purdue University, University of Nebraska-Lincoln, University of Arizona, University of California, Irvine.
Source of Support: NSF-DMREF
Website: none.
Keywords: Heusler alloy, Low barrier magnet (LBM), probabilistic-bit (p-bit)
Project Scope: The project aims to develop materials for designing p-bits for probabilistic computing at room temperature. It focuses on identifying novel soft magnetic Heusler alloys with ultra-low energy barriers and high-speed fluctuation rates, controlled by spin-orbit torque (SOT) materials. The approach includes applying p-bit theory, high throughput materials screening, first-principles calculations, wafer-scale combinatorial material synthesis, fast turnaround material and device characterizations. Key materials and devices studied are low-barrier magnets (LBMs) and magnetic tunnel junctions (MTJs), with a focus on Heusler alloys. Stochastic Landau-Lifshitz-Gilbert (s-LLG) models and p-bit device fabrication are being developed, aiming to demonstrate p-bits with fluctuation frequencies up to tens of GHz.
Relevance to MGI: Our team works in a closed loop fashion to integrate p-bit theory, high throughput materials screening, first-principles calculations, wafer-scale combinatorial material synthesis, fast turnaround material and device characterizations, and atom to system modular simulations, in order to accelerate materials discovery and lay the foundation for a probabilistic computer. During the first year of the program, we formed smaller loops to accelerate materials and device exploration. One subloop is to apply p-bit theory and stochastic LLG simulations to study the dynamics of magnetic p-bits as a function of experimentally variable material parameters. The conclusions and metrics are being used in first-principles calculations to quickly identify the materials candidates with ultra-low energy barriers. Another subloop is to characterize p-bit devices via diamond nitrogen vacancy (NV) center based high-resolution magnetometry and spin torque FMR**.** This loop analyzes the performance and further validates the materials design and synthesis by correlating it with the material characterization.
Technical Progress: Magnetic anisotropy induced by magnetoelastic coupling in randomly strained bits is the key obstacle for implementing low-barrier p-bit arrays. According to our estimates, for a typical p-bit volume (35 nm diameter, 3 nm thickness), the low-barrier condition $KV \sim kT$ (where K is the magnetic anisotropy energy and V the volume of the bit) requires the magnetoelastic constants, $B_1 \sim B_2 \sim 0.1$ MPa for random strain of order 0.5%. Toward addressing this material challenge, Co-PI Belashchenko is performing a high-throughput computational study of magnetoelastic coupling in multiple cubic compounds. More than 200 cubic compounds among Heusler alloys ($L2_1$, $C1_b$, and XA structures) and compounds with B2 and $D0_3$ structures are selected, and a high-throughput computational procedure to calculate B_1 and B_2 is developed and implemented for both LMTO (linear muffin-tin orbital method) and plane-wave-based pseudopotential (VASP) calculations. The requirement of $B_1 \sim B_2 \sim 0.1$ MPa is unlikely to be met by a choice of a single ordered compound. Among ~80 $L2_1$ compounds for which results are currently available, none have $B_1, B_2 < 2$ MPa.

Co-PI Wang's lab has configured a new deposition tool for high throughput MTJ growth. The tool is capable of combinatorial growth of Heusler materials with up to five different elements. Different wedge layers can be also deposited to form heterostructures. However, each time the composition of the targeted layers in the MTJ heterostructures will vary continuously across the entire 4" wafer, limiting the number of distinct MTJ stack to be only one during each fabrication cycle. Wang's lab has developed an in-situ mask index system that can be selectively applied during the growth of the targeted layers, exposing only 1/4 (1/6) the wafer. In this way, four (six) distinct MTJ stacks can be

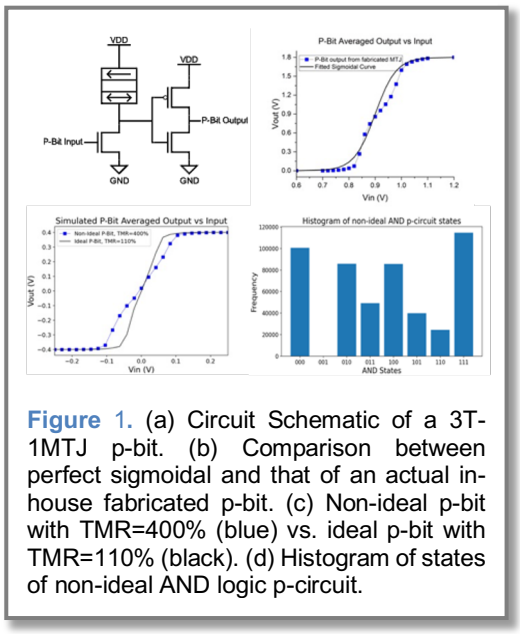


Figure 1. (a) Circuit Schematic of a 3T-1MTJ p-bit. (b) Comparison between perfect sigmoidal and that of an actual in-house fabricated p-bit. (c) Non-ideal p-bit with TMR=400% (blue) vs. ideal p-bit with TMR=110% (black). (d) Histogram of states of non-ideal AND logic p-circuit.

grown in one fabrication cycle, greatly increasing the throughput of MTJ fabrication. In addition, Wang has explored MTJ with antiferromagnetic electrode (AF-MTJs). According to Co-PI Upadhyaya's work, the fluctuation frequency in AF-MTJs can be substantially higher than that of MTJs based on ferromagnetic materials. Wang has fabricated full AF-MTJs with the core structure of $PtMn_3/MgO/PtMn_3$. Initial results have revealed that these AF-MTJs can be reversibly switched by SOT effects, with a critical current density in the range of 10^7 A/cm^2.

PI Chen, Co-PI Upadhyaya and Appenzeller at Purdue have been focusing on 1) fabrication and characterization of fast fluctuating stochastic CoFeB magnets by means of quantum sensing techniques based on Nitrogen-Vacancy (NV) centers; and 2) studying the impact of experimental non-idealities in the sigmoidal response of p-bits on various types of p-circuits. Upadhyaya's calculations show that the magnetic noise produced by the fluctuating probabilistic bits would dominate any intrinsic relaxation processes in the NV Center, even for sub-K_bT barriers [1]. Therefore, the T_1 time can be used as a nanoscale GHz spectrometer for probing fluctuating magnets. We have also started pursuing experimental characterization of p-bit materials via two complementary approaches for measurements. Appenzeller has built a compact implementation of a p-bit by integrating a stochastic MTJ with an access transistor and an inverter in a 3T-1MTJ configuration. It has been observed in our experiments that non-idealities in the stochastic MTJs – such as telegraphic fluctuations and a bimodal resistance distribution, as well as an excessively large tunnel magnetoresistance ratio (TMR) – can interact with the inverter's voltage transfer curve (VTC) to introduce plateaus to the output curve (whereby the tunability of the p-bit output in the intermediate stochastic region is diminished). To make it a non-ideal p-circuit, a TMR of 400% was introduced in SPICE simulations, and a comparison was made with an ideal circuit where MTJs had a TMR of 110%. **Figure 1** shows: At an individual p-bit level, plateaus similar to experimental demonstrations can be seen; At a circuit level, the frequencies of incorrect solution states are high, effectively making the circuit unusable.

Co-PI Krivorotov built and tested a setup of time-resolved magnetization dynamics in nanoscale MTJs that features an 80-ps time resolution. Time-resolved measurements of the auto-oscillations of magnetization driven by spin torque in a nanoscale MTJ in response to a 15-ns long current pulse have been demonstrated. And thermally-activated random spiking neuron signal was generated by a nanoscale MTJ in response to a direct current bias. Krivorotov lab has also developed a setup for rapid measurements of the angular dependence of broadband ferromagnetic resonance (FMR). The setup is fully automated and features automatic rotation of the film via 360° while measuring the FMR resonance field. These FMR measurements give direct information on magnetic anisotropy of ferromagnetic and ferrimagnetic films. We will use this setup for quantifying magnetic anisotropy in the LBM material candidates.

Future Plans: We will continue to accumulate the data for the chosen compounds. Once appropriate material systems are identified by the DFT calculations, Heusler alloy thin films and MTJ stacks will be fabricated. Optimization of AF-MTJs for p-bit application will be carried out. We will continue using confocal microscopy with NV center ensembles to provide quick feedback on LBM thin films. We have successfully won a user proposal from the CNMS at the OakRidge National Lab to access their AFM equipped with a diamond-based scanning NV tip. This project will allow us to measure the magnetic noise with a spatial resolution down to $\sim 20nm$. We will also extend our exploration of impact of non-idealities in the sigmoidal response of p-bits to higher level circuits while using a KL divergence metric for a thorough quantitative analysis. A major goal of this project is development of magnetic materials with low magnetostriction for integration into nanoscale p-bits. The new broadband FMR setup at UCI will allow us to rapidly characterize the angular dependence in FMR ferromagnetic films as a function of in-plane uniaxial strain and thereby identify materials with minimal strain-induced anisotropy.

Broader Impacts and Workforce Development: Wang has led a physics outreach event with a series of physics demonstrations for high school students. Purdue PIs are training undergraduate students at the interface of quantum sensing and microelectronics via a project-based course, titled "quantum sensing for new era microelectronics". Krivorotov has developed two new hands-on demonstration modules for a middle school outreach program at UCI: (i) a superconducting magnetically levitated vehicle and (ii) a miniature catapult.

Data Management and Open Access: We will create a publicly accessible database on spintronic properties of Heusler alloys. The database will be available via a dedicated website hosted at Purdue University. The database will contain both theoretically predicted (DFT) and experimentally observed properties, properly referenced to our own results as well as to data from literature and other online databases.

Advancing Along the Materials Development Continuum and Partnerships to Translation: In October of 2023, Krivorotov gave a seminar on the novel self-generated anomalous Hall spin-orbit torque to industrial researchers at the Western Digital Technologies Inc.

Publications and References

1. Konakanchi, S.T., Upadhyaya, P., "*Characterizing probabilistic bits with quantum spin defects*", Device Research Conference, Maryland, June 24-26, 2024
2. Belashchenko, K.D., "*Exchange-driven spin Hall effect in anisotropic ferromagnets*", Phys. Rev. B, **109**, 054409 (2024)
3. Eric Arturo Montoya, Xinyao Pei, and Ilya N. Krivorotov, *"Self-generated spin-orbit torque driven by anomalous Hall current"*, arXiv:2401.05006 (2024).
4. V. P. Amin, G. G. Baez Flores, A. A. Kovalev, K. D. Belashchenko, "*Direct and indirect spin current generation and spin-orbit torques in ferromagnet/nonmagnet/ferromagnet trilayers"*, arXiv: 2312.04538 (2023)

Machine-Assisted Quantum Magnetism

Lead Investigator: Sugata Chowdhury, sugata.chowdhury@howard.edu
Participating Institutions: Howard University, Northeastern University, SLAC, Stanford University
Website: https://physics.howard.edu/faculty-websites/sugata-chowdhury/
Keywords: Machine learning, quantum magnetism, quantum spin liquid, skyrmions, X-ray scattering.

Research Scope:

Strongly correlated electrons in quantum magnetism led to collective phenomena, such as emergent magnetic excitations and topological magnets. Efforts have been made to extend the limits of experimental tools for probing low-energy excitations in materials, as well as to integrate theoretical efforts aimed at comprehensive, material-specific modeling of experimental spectra. (1) Our systematic theoretical modeling effort implements first-principles, parameter-free, all-electron DFT-based computations to obtain the minimal, material-specific, effective tight-binding model Hamiltonian for effective spin interactions. (2) Experimentally measured spectral responses have been modeled to provide a range of parameter values of the Hamiltonian that encode the strength of electronic correlations, simulating the Hamiltonian using density-matrix renormalization group (DMRG) to capture the correlated magnetic states. (3) Machine-learning (ML) models have been developed to identify the parameters for the correct correlated model Hamiltonian that can accurately describe the experimental spectra. (4) When the Hamiltonians being considered are unable to describe the experimental spectra, we find an improved material-specific model Hamiltonian with more orbitals and higher-order overlaps to introduce correlation effects. (5) This cycle will be repeated until a satisfactory correlated Hamiltonian has been found that accurately describes the experimental spectra for a given material.

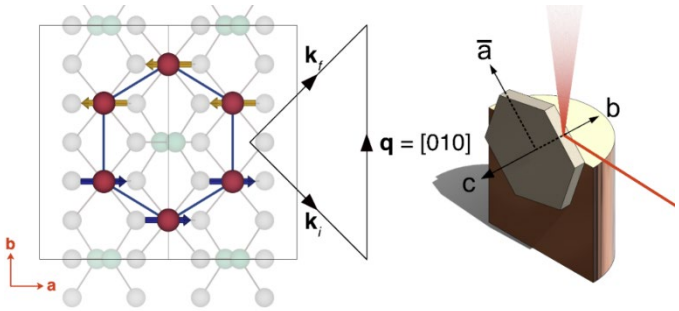
With a material-specific, correlated model Hamiltonian for a given material in hand, we are uniquely positioned to combine experimental evidence with theoretical modeling/computation and ML tools within a robust new integrated framework. Moreover, we have demonstrated the possibility of modeling, interpreting, and analyzing experimental data in real time, allowing adjustments in the multimodal experimental workflows as well as in theoretical models to make much more efficient use of the very expensive resources of the LCLS and significantly reduce the time to discovery for achieving scientific breakthroughs.

Our research scope is aligned with Topic 2: Collective phenomena in the current FOA [2], and addresses DOE's priority in data-driven approaches to prediction, discovery, and novel characterization of topological or magnetic quantum materials with phenomena dominated by electron correlations, entanglement, or interfaces.

Recent Progress

Van der Waals (vdW) magnetic materials are comprised of layers of atomically thin sheets, making them ideal platforms for studying magnetism at the two-dimensional (2D) limit. These

materials are at the center of a host of novel types of experiments, however, there are notably few pathways to directly probe their magnetic structure. We report the magnetic order within a single crystal of $NiPS_3$ and show it can be accessed with resonant elastic X-ray diffraction along the edge of the vdW planes in a carefully grown crystal by detecting structurally forbidden resonant magnetic X-ray scattering. We find the magnetic order parameter has a critical exponent of $\beta \sim 0.36$, indicating that the magnetism of these vdW crystals is more adequately characterized by the three-dimensional (3D) Heisenberg universality class. We verify these findings with first-principles density functional theory, Monte-Carlo simulations, and density matrix renormalization group calculations.



Magnetic unit cell of $NiPS_3$ viewed along the c-axis and X-ray scattering setup schematic showing the orientation of the crystal and copper mount with respect to the beam (shown in

This is a showcase of the point (1) and (2) out of all the five points listed in the scope section. Specifically, we perform two independent studies using first-principles DFT calculations, and these results are used to initiate additional theoretical calculations using DMRG and Monte Carlo simulations. Because there is a large discrepancy in the literature for the microscopic model of $NiPS_3$, we used first-principles density Functional Theory (DFT) to extract the magnetic exchange parameters using two different methods. We use the spin-1 Heisenberg model with exchanges J_1, J_2, J_3, and J_4 on the honeycomb lattice with single-ion anisotropy. For the Monte Carlo simulation of the bulk spin dynamics, the small interlayer exchange J_4 is included. The DMRG result confirms the stability of the magnetic structure in the single layer and that the magnetic exchange parameters yield a zig-zag order for the ground state measured here, with ferromagnetic chains along the a-axis and antiferromagnetic modulation along the b-axis with modulation vector q = [010]. The spins are canted slightly above and below the ab-plane. Although these types of Transition Metal Chalchogenophosphate materials are primarily thought to exhibit 2D magnetism due to their vdW structure, the critical exponent measured here, and confirmed with theory, is surprisingly consistent with the universality class of the 3D Heisenberg model. We have demonstrated that our experimental findings suggested a 3D Heisenberg-like spin Hamiltonian and that this model predicts a static ground state that is consistent with our data.

Future Plans

Based on our findings, we further investigate the microscopic origins of anisotropic spin interactions in this family of compounds. Surprisingly, we discovered that even in 3d transition metals such as Ni, where spin-orbit coupling (SOC) is typically negligible, heavy ligands with strong SOC can induce bond-dependent Kitaev interactions in Mott insulators like $NiPSe_3$. This generates Kitaev interactions analogous to those observed in other Kitaev candidate materials,

such as α-$RuCl_3$. We explore the potential to manipulate these anisotropic spin interactions and reveal that intriguing Kitaev physics emerges in the 3d-transition-metal chalcogenophosphate $NiPSe_3$. Through comparisons with similar systems exhibiting different levels of SOC, our insights offer a pathway to "engineer" Kitaev spin interactions in such materials. We could confirm these theoretical predictions through neutron scattering measurements.

This is a showcase of the point (1) and (4) out of all the five points listed in the scope section. The spin model for NiPS3 may not validate $NiPSe_3$, where pronounced SOC exists in ligand orbitals. Therefore, we investigated the origination of spin interactions and improved the material-specific model Hamiltonian with more orbitals and higher-order overlaps to introduce correlation effects. Interestingly, we found a method to tune the Kitaev interaction in the 3d transition metal van der Waals family of magnets. By comparing the two following systems: $NiPS_3$, where bond-dependent anisotropic spin interactions are absent from its microscopic description, and $NiPSe_3$, where a finite Kitaev spin interaction term can arise in its spin model, we determine how to create a sizable Kitaev interaction in the chalcogenophosphate materials based on nickel. Such an interaction term can arise if the Se p orbital, which mediates the superexchange between nearest-neighbor Ni sites, is subject to a pronounced SOC. The ground state in the spin model of $NiPSe_3$ is primarily attributed to the competition of the ferromagnetic nearest-neighbor coupling parameter J_1 and the antiferromagnetic third-neighbor Heisenberg coupling J_3. However, the lattice distortions show off-diagonal coupling terms in our microscopic spin model. By comparing the coupling strengths versus the SOC strength, we can predict the potential for further substitution of atoms to enhance the Kitaev term in candidate materials. By integrating this approach with machine learning models for materials structure predictions, we have demonstrated the capability to significantly broaden the range of potential Kitaev material candidates.

We are currently engaged in experimental efforts to validate the new model we proposed for $NiPSe_3$. Additionally, to analyze neutron scattering data, we plan to utilize our proprietary machine learning (ML) methodology to fine-tune model parameters. This ML approach, developed specifically for addressing points (3) and (5), will facilitate the identification of collective phenomena, as Kitaev materials are part of the broader category of topological magnets. Consequently, we will dedicate more time refining methods for observing topological excitations in $NiPSe_3$, such as magnon-phonon coupling.

Broader Impacts and Workforce Development: The project trains undergraduate, graduate, and postdoctoral students to pursue theoretical and experimental research in quantum materials, quantum information sciences, and data-driven analysis. A special feature of this project due to its location at Howard University, which is a leading HBCU, is that it directly impacts the training of underserved communities for careers in the quantum workforce for the industries of tomorrow. The project is also helping to improve the quantum infrastructure at Howard University, which will continue to impact the ability of the university for the quantum training of minorities long after the project has ended.

Data Management and Open Access: Individuals involved in this project review and valivalidate collected data at all research stages to ensure that the analytical data is transcribed correctly to the correct reporting format. Data are summering into the appropriate digital format. Any computations performed in this project are explicitly written,n showing all steps and equations used in the calculations; brief explanations will accompany the calculations where necessary. These calculations, experimental results, and notes are attached to and always accompanied by the raw data. The collected data have been submitted for publication to peer-reviewed journals and appropriate conferences throughout and upon completion of the research. We have already developed a project webpage that will be maintained throughout the project's life.

Advancing Along the Materials Development Continuum and Partnerships to Translation: The success of this research proposal will not only significantly accelerate the material discovery and exotic quantum states but also deepen our understanding of the interlay of nontrivial topology magnetism and electron correlations. Our team, with world-leading experts from material prediction and synthesis to measurements, can make the subject of quantum magnetism a well-planned and integrated educational opportunity for the students and general public: (1) We are holding a bi-weekly virtual team meeting. Students present their recent progress in this meeting and discuss the literature turns with common interests. Through this, we work as a team, and students can learn from others outside their fields. (2) PI Chowdhury has been actively involved in designing new courses on quantum materials at Howard University in collaboration with IBM. As the COVID-19 restriction is easing out, the PI and Co-PIs plan to design summer workshops at Howard University for middle and high school students to bring awareness to this novel nanotechnology education.

Publications

1. Rajan Plumley, Sougata Mardanya, Cheng Peng, Johannes Nokelainen, Tadesse Assefa, Lingjia Shen, Nicholas Burdet, Zach Porter, Alexander Petsch, Aidan Israelski, Hongwei Chen, Jun Sik Lee, Sophie Morley, Sujoy Roy, Gilberto Fabbris, Elizabeth Blackburn, Adrian Feiguin, Arun Bansil, Wei-Sheng Lee, Aaron Lindenberg, Sugata Chowdhury, Mike Dunne, Joshua J Turner, *3D Heisenberg universality in the Van der Waals antiferromagnet $NiPS_3$*, DOI link: https://doi.org/10.48550/arXiv.2310.07948
2. Skyrmions: A review on materials perspective for future electronic devices; Vineet Kumar Sharma, Alana Okullo, Jalen Garner, Cheng Peng, Rajan Plumley, Adrian Feiguin, A. Bansil, Josh Turner, and Sugata Chowdhury, Invited article under review.
3. Kitaev physics in the two-dimensional magnet NiPSe3, Cheng Peng, Sougata Mardanya, Alexander Petsch, Vineet Kumar Sharma, Shuyi Li, Chunjing Jia, Arun Bansil, Sugata Chowdhury, and Joshua J. Turner; arXiv:2403.09831; 2023, Under Review Phys. Rev. Lett. Impact factor 9.161.
4. Topological Hall effect induced by chiral fluctuations in a kagome lattice; Kyle W. Fruhling, Alenna Streeter, Sougata Mardanya, Xiaoping Wang, Priya Baral, Oksana Zaharko, Igor I. Mazin, Sugata Chowdhury, William D. Ratcliff, Fazel Tafti, arXiv:2401.17449, Under review Phys Rev Mat.
5. 3D Heisenberg universality in the Van der Waals antiferromagnet NiPS3, Rajan Plumley, Sougata Mardanya, Cheng Peng, Johannes Nokelainen, Tadesse Assefa, Lingjia, Shen, Nicholas Burdet, Zach Porter, Alexander Petsch, Aidan Israelski, Hongwei Chen, Jun Sik Lee, Sophie Morley, Sujoy Roy, Gilberto Fabbris, Elizabeth

Blackburn, Adrian Feiguin, Arun Bansil, Wei-Sheng Lee, Aaron Lindenberg, Sugata Chowdhury, Mike Dunne, and Joshua J. Turner, arXiv:2310.07948, Under review npj Quantum Materials. Impact factor 5.7.

6. The Case for a Defect Genome Initiative, Qimin Yan, Swastik Kar, Sugata Chowdhury, and Arun Bansil, Advanced Materials, Adv. Mater.2023, 2303098, Impact factor 29.4.
7. Unconventional superconducting pairing in a B20 Kramers Weyl semimetal; Sougata Mardanya, Mehdi Kargarian, Rahul Verma, Tay-Rong Chang, Sugata Chowdhury, Hsin Lin, Arun Bansil, Amit Agarwal, Bahadur Singh; arXiv preprint arXiv:2309.05880, 2023. Under Review Phys. Rev. Lett. Impact factor 9.161.
8. On Ultrafast X-ray Methods for Magnetism, Rajan Plumley, Sathya Chitturi, Cheng Peng, Tadesse Assefa, Nicholas Burdet, Lingjia Shen, Alex Reid, Georgi Dakovski, Matthew Seaberg, Frank O'Dowd, Sergio Montoya, Hongwei Chen, Alana Okullo, Sougata Mardanya, Stephen Kevan, Peter Fischer, Eric Fullerton, Sunil Sinha, William Colocho, Alberto Lutman, Franz-Joseph Decker, Sujoy Roy, Jun Fujioka, Yoshinori Tokura, Michael P. Minitti, Jeremy Johnson, Matthias Hoffmann, Michaela Amoo, Adrian Feiguin, Chuck Yoon, Jana Thayer, Yousseff Nashed, Chunjing Jia, Arun Bansil, Sugata Chowdhury, Aaron Lindenberg, Mike Dunne, Elizabeth Blackburn, Joshua Turner, Invited Paper arXiv:2305.07787 (2023), under review Advanced of Physics X, Impact factor 8.526.
9. Capturing dynamical correlations using implicit neural representations, Sathya Chitturi, Zhurun Ji, Alexander Petsch, Cheng Peng, Zhantao Chen, Rajan Plumley, Mike Dunne, Sougata Mardanya, Sugata Chowdhury, Hongwei Chen, Arun Bansil, Adrian Feiguin, Alexander Kolesnikov, Dharmalingam Prabhakaran, Stephen Hayden, Daniel Ratner, Chunjing Jia, Youssef Nashed, Joshua Turner, arXiv:2304.03949, Nature Comm. 14, 5852, 2023, Impact factor 16.6.
10. Machine learning enabled experimental design and parameter estimation for ultrafast spin dynamics, Zhantao Chen, Cheng Peng, Alexander N. Petsch, Sathya R. Chitturi, Alana Okullo, Sugata Chowdhury, Chun Hong Yoon, Joshua J. Turner, Mach. Learn.: Sci. Technol. 4 045056., 2023, Impact factor 6.8.
11. Intrinsic magnetic topological phases in MnBi2Se4; Baokai Wang, Anan Bari Sarkar, Gyanendra Dhakal, Madhab Neupane, Amit Agarwal, Arun Bansil, Sugata Chowdhury, and Bahadur Singh. (In-preparation)
12. Intrinsic magnetic topological phases in MnBi2Se4; Baokai Wang, Anan Bari Sarkar, Gyanendra Dhakal, Madhab Neupane, Amit Agarwal, Arun Bansil, Sugata Chowdhury, and Bahadur Singh. (In-preparation)
13. On the Role of Defects in the Electronic Structure of MnBi2-xSbxTe4; D. Nevola, Kevin F. Garrity, N. Zaki, J.-Q. Yan, H. Miao, Sugata Chowdhury, and P. D. Johnson (under review). arXiv:2206.14325
14. Testing the data framework for an AI algorithm in preparation for high data rate X-ray facilities, Hongwei Chen, Sathya R. Chitturi, Rajan Plumley, Lingjia Shen, Nathan C. Drucker, Nicolas Burdet, Cheng Peng, Sougata Mardanya, Daniel Ratner, Aashwin Mishra, Chun Hong Yoon, Sanghoon Song, Matthieu Chollet, Gilberto Fabbris, Mike Dunne, Silke Nelson, Mingda Li, Aaron Lindenberg, Chunjing Jia, Youssef Nashed, Arun Bansil, Sugata Chowdhury, Adrian E. Feiguin, Joshua J. Turner, Jana B. Thayer, 2022 4th Annual Workshop on Extreme-scale Experiment-in-the-Loop Computing (XLOOP), Dallas, TX, USA, 2022, pp. 1-9, doi: 10.1109/XLOOP56614.2022.00006.

DMREF: Discovery, Development, Design and Additive Manufacturing of Multi-Principal-Element Hexagonal-Close-Packed Structural Alloys

Lead Investigator: Daryl C. Chrzan, dcchrzan@berkeley.edu
Participating Institutions: University of California, Berkeley; Lawrence Livermore National Laboratory, Livermore; Laney College, Oakland
Source of Support: NSF-DMREF
Website: none
Keywords: Multi-principal-element HCP structural alloys; additive manufacturing; cryogenic structural materials
Project Scope

This DMREF project pursues data-driven discovery, development, design and additive manufacturing of hexagonal-close-packed (HCP) multi-principal-element alloys (MPEAs) intended for use at room temperatures and below. The program will couple high-throughput computation, high-throughput experiment, and data science methods, to rapidly identify ductile, high specific-strength structural MPEAs with the nominal HCP structure. The synthesis work will be carried out using conventional casting/forging and additive manufacturing to ensure that the discovered alloys can be rapidly incorporate d into emerging technologies.

Relevance to MGI

A key challenge in alloy design is correlating accessible descriptors (both computed and observed) to alloy mechanical performance. Our approach involves a reliance on the methods of machine learning to quantify the correlations between composition, processing parameters, and structural properties.

Specifically, we have identified descriptors, both computable and observable, that will be used to inform machine learning models that will, in turn, guide our exploration of composition space and processing parameters for optimizing alloy performance. The chosen computable descriptors have already been shown to correlate with differing mechanical responses (e.g. encouraging ⟨c+a⟩ slip vs. twinning), whereas the observable descriptors focus on observing the true mechanical response of the alloys.

Technical Progress

We are exploring the properties of HCP-MPEAs formed from Ti, Hf, Zr, Y, and Sc due to their crystallization in the HCP structure and their wide range of properties (e.g., c/a ratios) and interactions (mixing vs. segregating), which show significant potential for producing HCP alloys. For our initial compositional exploration, we focused on the Ti-Zr-Hf equiatomic system. The CALPHAD predicted pseudo-binary phase diagram for this alloy system has a liquidus point around 2000K and is expected to form a BCC structure below this temperature. Upon further cooling to approximately 1300K, a stable HCP solid solution is predicted. Remarkably varying the Ti content maintains the overall phase composition.

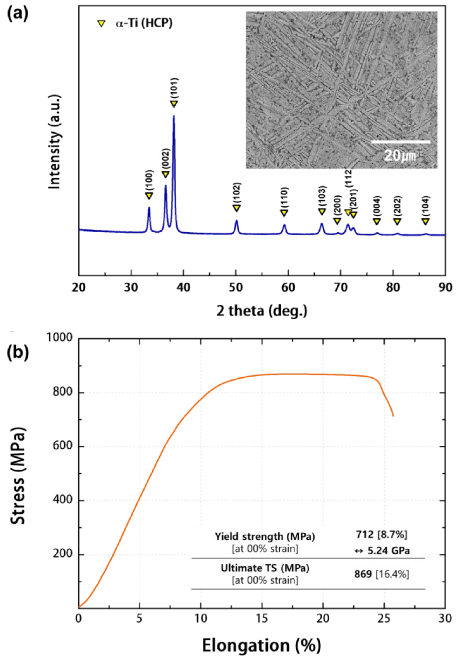


Figure 1. Microstructure of equiatomic Ti-Zr-Hf alloy (a) XRD trace and SEM image (inset) (b) Tensile stress-strain curve.

We synthesized an equiatomic ternary alloy using arc-melting, and the resultant microstructure is shown in **Fig. 1**. As indicated in Fig. 1(a), the arc-melted Ti-Zr-Hf alloy exhibited a fully HCP structure. However, the SEM image in the inset reveals that the HCP phase formed in a martensitic structure (lath type), likely due to the rapid solidification process. An intriguing aspect of this alloy is its exceptional ductility despite having a fully martensitic HCP phase. Fig. 1(b) shows a tensile test result of this alloy, which demonstrated an impressive strength exceeding 700 MPa and an elongation of over 27% at fracture. This level of strain is unusual for martensitic structures with

limited slip systems, highlighting the alloy's significant research potential. Going forward, we will expand the experimental alloy system to a wider range of compositions and carefully characterize the microstructural changes and the underlying formation mechanisms associated with varying compositions at both room and cryogenic temperatures.

In our computational efforts, we have developed the strategy that we will employ to create our machine learning empirical potential, and begun its implementation. Briefly, we have discovered that the properties of multicomponent alloys can be predicted reasonably well based on computations of the properties of all the relevant binaries. So, for our five component system, we can focus on computing the properties of 10 binary alloy systems using DFT, and construct our initial interatomic potential based on these results.

Future Plans

Plastic deformation in HCP alloys is often highly anisotropic resulting in reduced ductility. However, there are several effects arising from the disorder in MPEAs that will allow us to tune the plastic anisotropy of the alloys, and thereby optimize their structural properties for specific applications. Our immediate plan is to develop the connections between computable and observable descriptors using arc-melted samples and high-throughput computation. Our initial investigations suggest that currently available universal machine learning interatomic potentials (MLIPs) do not provide sufficient accuracy for structural properties to enable the goals of the research. So we are pursuing the development a MLIP tuned specifically for the HCP metals Ti, Zr, Hf, and eventually also Y and Sc. With this MLIP, we will compute all of the identified computable descriptors (e.g. c/a, elastic constants, twinning stress, stacking fault energies, etc.) as a function of alloy composition.

Simultaneously, we will further the development of a samples for structural, phase-stability and mechanical property characterization, using x-ray diffraction, differential scanning calorimetry, scanning and transmission electron microscopy, nanoindentation and cyrogenic nanoindentation. This data will be curated and used to improve the machine learning algorithm. Together, the experimental and computable observables will narrow the compositions to be studied using additive manufacturing. In the latter stages of this work, we plan to focus extensively on transitioning the understanding we obtained from arc-melted samples into the additive manufacturing framework where we will expand our data set to include processing parameters. This model, then, will be used to develop ductile HCP-MPEAs with high specific strength.

Broader Impacts and Workforce Development

Our program involves a number of scholars at varying stages in their academic careers. First, we are hosting two undergraduates from the welding program at Laney College (a local community college). These interns will support our arc melting efforts. We have one UCB undergraduate student participating in an LLNL internship program focused on MPEAs. Second, we have a number of graduate students that are involved in the research, including 3 funded by this program, and others with similar interests on fellowship, or funded by other research efforts. This group includes six students in UC Berkeley's Masters of Engineering program that worked on characterizing additively manufactured MPEAs obtained from paste printers. These six students now work in industry using their learned skills.

Data Management and Open Access

The strategy for data management and open access will include making computed data available to the community using resources developed by our collaborators in the Materials Project. At this stage there is not sufficient data to warrant dissemination, but this will be a key area of effort as the project matures.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Our project uses machine learning to identify the correlations that are necessary for the design of improved HCP-MPEAs for low-temperature applications. While the models we are developing will initially be geared towards the additive manufacturing of HCP-MPEAs for low temperature applications, the approach should be readily extendable to other crystal structures. Our intent is to patent any intellectual property that arises from our research, and to seek pathways to bring the technology to market.

Publications and References

None yet.

MaterialsTube.org

Lead Investigator: Vincent Crespi, vhc2@psu.edu
Participating Institutions: The Pennsylvania State University
Source of Support: NSF-MIP
Website: www.2dccmip.org, www.materialstube.org
Keywords: Knowledge sharing, video, software infrastructure, AI, large language models.

Project Scope

Workshops, seminars, and summer schools on materials research and development provide a major channel of education and training for the MGI workforce, yet these resources are currently fragmented with practical barriers to making them more systematically accessible and discoverable. MaterialsTube.org aims to ease the task of extracting, curating, hosting, and discovering video content and metadata for workshop/seminar/summer school presentation/discussion videos and also materials instrumentation training videos, in a community video database.

Relevance to MGI

A key component of the iterative feedback loop for MGI-inspired materials research and development is the deployment at the community level of knowledge sharing mechanisms that disseminate discoveries along the MGI continuum and more specifically to enhance the findability and discoverability of the component of the fundamental MGI knowledge base that takes the form of video content. Machine learning and AI tools have a natural place here in extracting video metadata such as speakers and topics (facilitated by audio transcript extraction tuned to a materials vocabulary) and also in providing discovery tools for content of interest to specific users. In this manner, MaterialsTube harnesses the power of data in the specific form of materials research presentation and discussion video content.

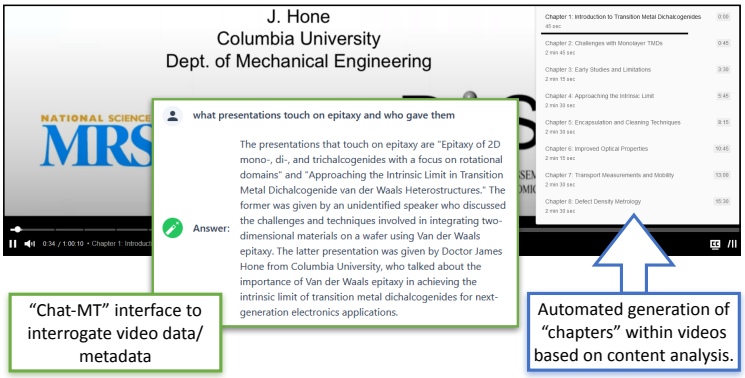


Figure 1: Depiction of automatic video chapterization with an overlay showing the chatbot search and summarization interface.

Technical Progress

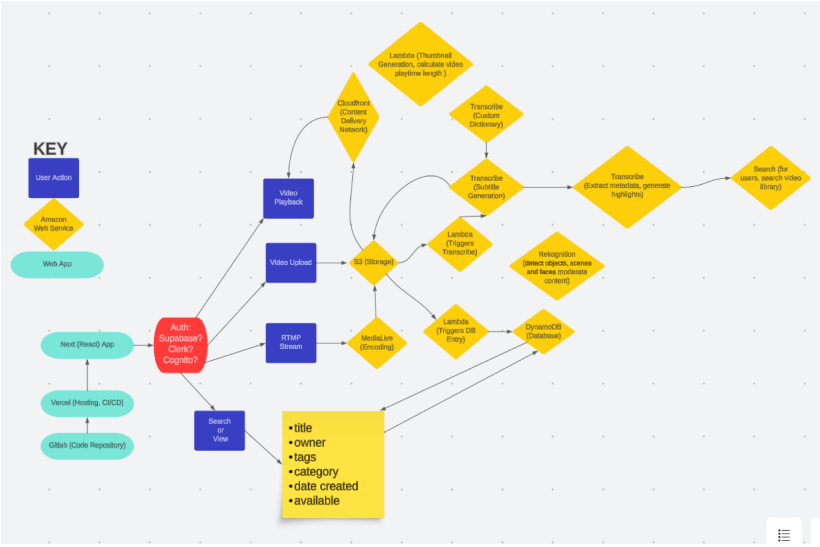


Figure 2: Framework of interactions between components of MaterialsTube.

A baseline implementation of MaterialsTube.org has been created, with drag-and-drop video upload with AI-enabled transcript extraction and video chapterization. Filtering to remove personal identifying information and inappropriate content is in place. Video upload, search, and playback are functional. A chatbot interface is under development and optimization. User account management and real-time video stream ingestion are being scoped and refined. Note that the generative component of AI tools used by MaterialsTube is primarily in service of summarization and video discovery; the "ground truth" is the videos themselves, which acts to mitigate concerns on potential AI hallucinations of materials research content.

Software development for MaterialsTube.org has been performed by Frank Santaguida with management oversight by Kevin Dressler.

Future Plans

MaterialsTube will become publicly available in beta form when user account management is completed, with a set of seed video content. Contingent on resource availability, future plans may include (1) addressing feedback during early community use of the beta product, (2) enhancing the functionality in terms of search, video subscriptions, commenting, video metadata curation and ingestion, single sign-on, and AI tools, (3) optimizing chatbot performance, (4) encouraging community uptake in terms of video upload and search use, which will require bootstrapping, (5) developing a plan towards the longer-term sustainability of the platform. The practicality of direct links from chatbot output to referenced videos is currently in an exploratory phase.

Broader Impacts and Workforce Development

A primary goal of MaterialsTube.org is to facilitate the education and training of the materials research and development workforce through an enhanced interface to video content related to materials research, including seminars, workshops, summer schools, and tutorials, i.e. a "one-stop shop" for the sharing, discovery, and viewing of materials-related video content. In addition to traditional discovery tools, large language models and other AI tools are being explored and adapted to knowledge discovery in this context. For example, the MaterialsTube upload system automatically chapterizes videos (recognizing changes in speaker and changes in topic within a given speaker's presentation) and extracts audio transcripts (pre-trained on materials-related vocabulary). These value-added features are intended to make MaterialsTube a compelling platform choice for materials-related user video content by both saving time, effort, and resources on behalf of workshop/summer school/seminar organizers and by providing a platform for enhanced discovery of materials-related video content.

Data Management and Open Access

By design, MaterialsTube is a delivery vehicle to support the application of FAIR principles to materials data in the form of seminar, workshop, and summer school videos. Videos uploaded to MaterialsTube.org will be publicly accessible to the entire community. Natural language processing is used to generate video transcripts that are searchable and interrogatable through both traditional keyword search or via a chatbot interface. Additional semantic elements of video content could be extracted by machine vision analysis of videos. Video content is thereby made findable and accessible. In terms of video upload, interoperability is currently implemented as a simple drag-and-drop interface; direct video streaming input using open protocols is currently under development. Videos are displayed using widespread open protocols. Due to issues of server load and anticipated patterns of user usage, the system does not currently have an automated/API means of video download.

Advancing Along the Materials Development Continuum and Partnerships to Translation

MaterialsTube aims to accelerate materials discovery, development and deployment by facilitating knowledge transfer amongst practitioners and by enhancing workforce education and training in MGI-related skills, practices, and knowledge. These impacts are agnostic across materials, devices, and research methodologies. For broad impact, community uptake of the platform is essential, for both video upload and search/use. MaterialsTube is hosted by the Two-Dimensional Crystal Consortium, which provides a much-needed framework for (1) sustained IT development, maintenance, and support, (2) initial video content and (3) access to an initial community of users. The platform is not yet at a stage of development where commercialization is appropriate to be explored. Partnerships with video content producers and user community organizations may be explored in the future; these would likely focus on growing the userbase and database.

Publications and References

As a software infrastructure project in active development, the project has not yet produced publications. As the userbase and database grows, there may be opportunities for publication in disciplinary journals and broader venues.

DMREF/Collaborative Research/GOALI/: High-Affinity Supramolecular Peptide Materials for Selective Capture and Recovery of Proteins

Lead Investigator: Honggang Cui; Email: hcui6@jhu.edu
Participating Institutions: The Johns Hopkins University, University of Chicago, Northwestern University, Bristol-Myers Squibb
Website: none
Other PIs: Matthew Tirrell, University of Chicago; Monica Olvera de la Cruz, Northwestern University; Xuankuo Xu, Bristol Meyers Squibb
Keywords: supramolecular materials; high-affinity materials; protein purification; phase separation, protein binding.

The separation and purification of therapeutic proteins from their biological resources pose a great limitation for industrial manufacturing of biologics in an efficient and cost-effective manner. Despite the high media cost and limited loading capacity, affinity chromatography remains the most widely used capture method for large-scale industrial protein purification. The rapid growth of upstream titers, due to advancements in mammalian cell culture and continuous process development, has further challenged the efficiency of downstream manufacturing. This DMREF/GOALI proposal aims to develop a peptide-based platform technology for non-chromatographic protein purification, with the ultimate goal of addressing the inherent production limit of affinity chromatography.

Project Scope

Our long-term goal is to develop a peptide-based platform technology for non-chromatographic purification of proteins and other biologics. The objective of this research is to lay out the foundation for this platform technology through the development of high-affinity supramolecular immunofibers (IF) for selective capture and recovery of monoclonal antibodies (mAbs). Three specific aims have been set, each covering a key step toward the successful development of a non-chromatographic protein purification technology: (1) selective capture, (2) phase separation, and (3) protein recovery (**Fig. 1**). We envision that upon further computational and experimental optimization of our molecular, supramolecular and materials designs, the supramolecular peptide materials developed under this support can indeed serve as an efficient and economical alternative to traditional chromatography methods for purification mAbs and other proteins.

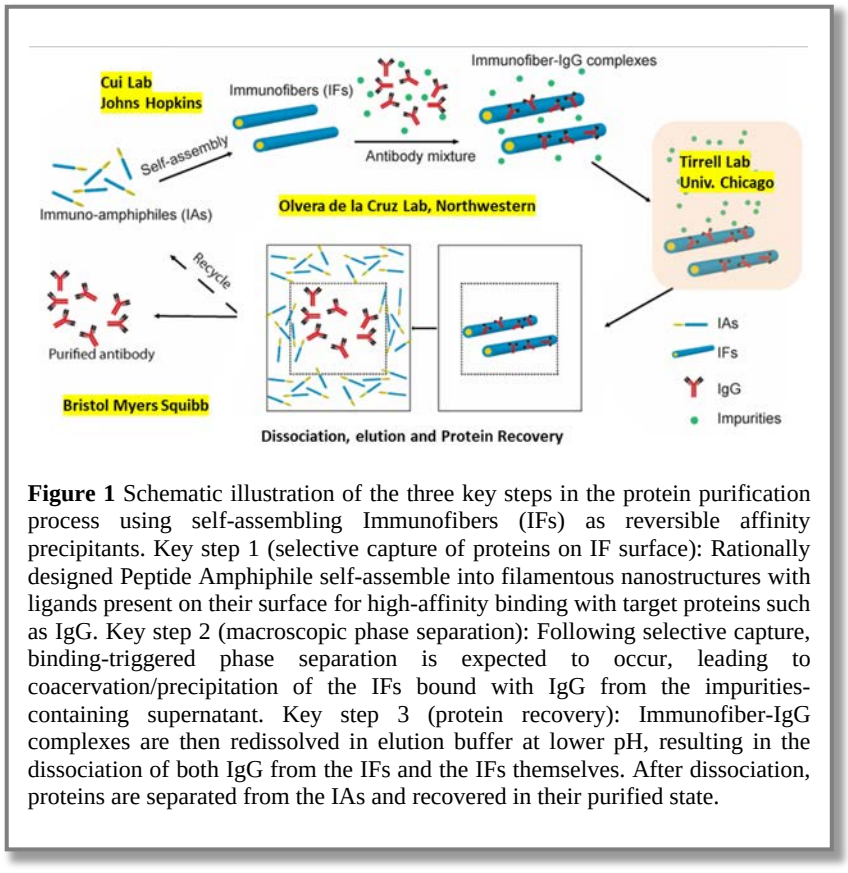


Figure 1 Schematic illustration of the three key steps in the protein purification process using self-assembling Immunofibers (IFs) as reversible affinity precipitants. Key step 1 (selective capture of proteins on IF surface): Rationally designed Peptide Amphiphile self-assemble into filamentous nanostructures with ligands present on their surface for high-affinity binding with target proteins such as IgG. Key step 2 (macroscopic phase separation): Following selective capture, binding-triggered phase separation is expected to occur, leading to coacervation/precipitation of the IFs bound with IgG from the impurities-containing supernatant. Key step 3 (protein recovery): Immunofiber-IgG complexes are then redissolved in elution buffer at lower pH, resulting in the dissociation of both IgG from the IFs and the IFs themselves. After dissociation, proteins are separated from the IAs and recovered in their purified state.

Relevance to MGI

The project aims to design, synthesize, and develop a new class of self-assembling peptide materials that can specifically bind, selectively capture, and effectively separate proteins from their bio resources. To address the key

fundamental challenges in materials design and development, an interdisciplinary research team is assembled, including computational, theoretical, and experimental expertise.

Technical Progress

We have successfully designed and synthesized mAb-binding peptide amphiphiles that can self-assemble into filamentous nanostructures (immunofibers) capable of capturing mAbs with high-binding affinity. We also demonstrated the significant use of these immunofibers for mAb separation and recovery. For instance, we designed a series of new IF building blocks by incorporating various oligo(poly)ethylene glycol (OEG or PEG) linkers to improve the presentation of mAb-binding peptides on the immunofiber (IF) surface. Our results suggest that increasing the linker length can significantly impact mAb-IF interactions and subsequent mAb precipitation yield. However, excessively long linkers have an adverse effect on the function of the resultant supramolecular polymers. By optimizing several key parameters that impact mAb-IF complexation, we demonstrated that the desired IF system could precipitate mAbs at high titers under no-salt conditions with promising yields. Computational methods were used to validate and explain our experimental findings. This new type of immunofiber could potentially be applied to the purification of mAbs from clarified cell culture harvests. We believe these results shed light on the development of high-affinity supramolecular constructs for specific molecular recognition.

Additionally, we performed important studies on the phase separation behavior and mechanisms promoted by the formation of immunofiber and mAb complexes. While phase separation driven by electrostatic interactions among polymers and polymer-protein complexes has been examined in various polyelectrolyte complexation systems, protein coacervate systems driven by high-affinity interactions in a low-salt environment have received less attention. Our studies suggest that the interactions between mAbs and supramolecular polymers (SPs) composed of filler and high-affinity ligand molecules can lead to coacervate formation followed by phase separation without the addition of salts. Theoretical and multiscale models have also been developed to provide important insights into the observed coacervation behavior. The scope of this work sheds new light on affinity-based coacervation systems in a minimal salt environment and improves our understanding of capturing mAbs for protein purification and therapeutic delivery applications.

Future Plans

We are in the process of preparing several important manuscripts based on our recent research findings. Simultaneously, we are evaluating the possibility of scaling up our system for industrial-level operations in collaboration with our industry partners.

Broader Impacts and Workforce Development

Through our unique tetrahedral collaboration between Johns Hopkins University, the University of Chicago, Northwestern University, and Bristol-Myers Squibb (BMS), we have created a diverse and inclusive working environment for graduate students, undergraduate students, high school students, and postdoctoral researchers. Undergraduate students are given the opportunity to work in different research institutions, experiencing a variety of laboratory settings and cultures. We have leveraged our research resources to offer meaningful research opportunities to individuals from underrepresented and historically marginalized backgrounds. Additionally, our collaborative efforts have facilitated interdisciplinary training and mentorship, fostering a generation of scientists equipped with a wide range of skills and perspectives. This initiative not only advances scientific knowledge but also promotes equity and inclusion in STEM fields, contributing to the development of a diverse and talented workforce.

Data Management and Open Access

We have established a OneDrive folder for seamless data sharing among the four research labs involved in this collaborative project. This centralized repository ensures that all team members have easy access to the latest data, fostering transparency and facilitating collaborative analysis. We are committed to publishing all meaningful results in reputable scientific journals.

Advancing Along the Materials Development Continuum and Partnerships to Translation

By collaborating among three research groups and an industrial partner, we are able to leverage our combined expertise to understand the capture mechanisms and phase separation behavior between proteins and engineered filamentous nanomaterials from both computational and experimental perspectives. This synergy fosters a dynamic learning environment that not only enhances our research capabilities but also streamlines the transition of our findings into industrial applications. Such a partnership ensures that our research efforts have a tangible real-world impact, bridging the gap between academic innovation and practical implementation.

Publications and References

1. Haque Pial, T.; Li, Y.; Olvera de la Cruz, M., Microscopically segregated ligand distribution in co-assembled peptide-amphiphile nanofibers. *Soft Matter* **2024,** *20* (23), 4640-4647.

2. Li, Y.; Kim, M.; Pial, T.; Lin, Y.; Cui, H.; Olvera de la Cruz, M., Aggregation-Induced Asymmetric Charge States of Amino Acids in Supramolecular Nanofibers. *The Journal of Physical Chemistry B* **2023,** *127* (38), 8176-8184.

3. Wang, H.; Su, H.; Xu, T.; Cui, H., Utilizing the Hofmeister Effect to Induce Hydrogelation of Nonionic Supramolecular Polymers into a Therapeutic Depot. *Angewandte Chemie International Edition* **2023,** *62* (43), e202306652.

Iterative Design and Fabrication of Hyperuniform-Inspired Materials for Targeted Mechanical and Transport Properties

Lead Investigator: Karen Daniels, kdaniel@ncsu.edu
Participating Institutions: NC State University, UNC Chapel Hill, UCLA, Johns Hopkins University
Source of Support: NSF-DMREF
Website: https://dmref.org/projects/339
Keywords: metamaterials, transport, disorder, network science

Project Scope: Open lattice structures are an exciting class of materials with better strength-to-weight and stiffness-to-weight ratios than bulk solids. We aim to develop novel approaches to design a new class of disordered metamaterials that are inspired by the predicted special transport properties (*e.g.* heat transfer and diffusion) of hyperuniform structures. Hyperuniform materials have slowly-growing density variations relative to the volume when the volume becomes sufficiently large. We will create additive-manufacturing (AM) techniques to produce samples, perform experiments to transport through the samples, and develop new modeling approaches (*e.g.* network analysis to create design heuristics and higher-order stochastic spatial-averaging techniques to account for microscale heterogeneity).

Relevance to MGI: We are developing *structure–process–property relations* to optimize the mechanical and transport properties of open-lattice disordered metamaterials such as those in Fig 1. We are integrating theory, computation, and experiment by reducing the problem to heuristics based on network measures, which will provide feedback to the generation of optimized configurations. The MGI approach is necessary due to the large parameter space: print orientation and powder structure at the microscale, network configuration at the mesoscale, and print material at the macroscale. By co-optimizing mechanical and transport properties, our team will use structure–property relationships to target optimization via the micro-, meso-, or macro-scales.

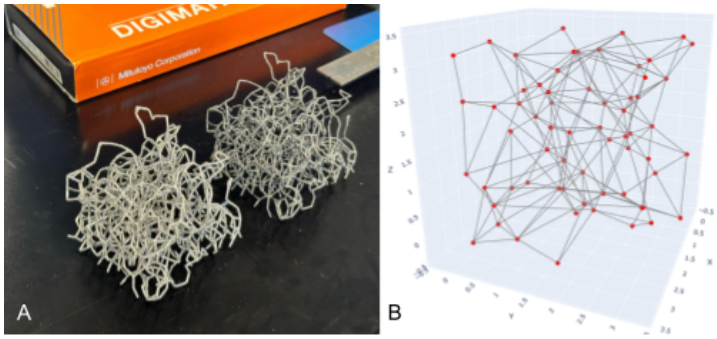


Figure: (A) Two successful metal prints of the type of disordered metamaterials studied in this project. The structure comes from the contact network of a granular packing as a manufacturing demonstration. The sample on the left is fabricated from Ti-6Al4V using electron beam powder bed fusion with no supports. The sample on the right is fabricated from 17-4PH steel using laser powder bed fusion with minimal supports. (B) A numerically generated structure with tunable disorder created from a Gabriel tessellation of the point cloud.

Technical Progress: The manufacturing team is working to optimize manufacturing methods of the 2D and 3D samples, experimentalists are using these for method development and to deploy new characterization capabilities, and theorists are exploring different algorithms to create and connect point clouds into printable structures and examine different network characterizations to explain trends in effective resistance. To tackle the challenge of printing unconventional complex 3D network designs, we have utilized polymer prototyping before moving to metal prints. We have developed techniques to measure geometry and print idealized angles and connecting rods to determine support requirements; this yielded process and support modifications. We have performed successful optical imaging, laser scanning, and X-ray tomography of these printed 3D geometries of different sizes, and converted the outputs to various 3D image formats for geometry analysis. We are using both images of as-built prints and theoretical network structures to develop finite-element "digital twins" of the structures. Ongoing characterization of both physical and numerical samples will inform the theorists of physical versus theoretical network edge quality. High-resolution X-ray tomographic imaging to characterize print quality provides feedback to the manufacturing team about overall build quality. By using prototype 2D networks that span from disordered to ordered configurations, we have achieved a key validation: an equivalence between numerically-simulated effective resistance and experimentally-measured resistance without any fitting parameters. Our numerical computations have revealed nontrivial behavior of the effective resistance as a function of the amount of disorder, including a dependence on the directionality of the measurement that we are actively

analyzing. We have also explored a variety of algorithms and spatial-network models — predominantly in 2D thus far, but recently with extensions to 3D — to create network structures from point clouds, controllably tune and measure the amount of disorder, and calculate network diagnostics to measure the properties of these structures.

Future Plans: With our advances in manufacturing and development of a database of numerical techniques to create hyperuniform and nearly-hyperuniform configurations (with tunable disorder), we are ready to begin the next iterative design phase while increasing experimental capabilities and simultaneously developing new theoretical methods to characterize the structures and predict their transport properties. This database includes both 2D configurations (which are easier to characterize in experiments) and 3D configurations (which are more realistic as materials). Focusing on three approaches — using Lloyd's algorithm, perturbed crystalline lattices, and jammed packings — we will print a subset of configurations from each of them in both metal and polymer feedstock. Informed by the results from the high-resolution X-ray tomography, the manufacturing team will improve 3D manufacturing geometry and microstructure control in multiple material systems, including alloy design, which will require the development of multiscale characterizations.

Our next characterization phase will develop techniques to measure the propagation of acoustic signals using a scanning-laser Doppler velocimeter. Starting with polymer samples, we will measure transmission efficiency as a function of frequency and amount of disorder (approaching hyperuniformity), and identify the role of both localized and non-localized modes. Comparison will be made to existing thermal and electrical measurements. We will continue developing finite-element digital twins, simulate mechanical and transport properties to validate against experiments, and then feed them back to the manufacturing team to improve the understanding of as-built versus theoretical properties and improve the print quality through print-parameter optimization.

We will analyze topological and geometric structures of 2D and then 3D configurations, including how these structures differ for different types of hyperuniform and related structures (near-hyperuniform structures, stealthy hyperuniform structures, etc.), how they depend on experimental parameters, and how they are affected by perturbations, noise, and manufacturing errors. We will develop new methods (*e.g.* network curvature and topological data analysis) which will give insight into a network-based definition of hyperuniformity and structure–process–property relations.

Broader Impacts and Workforce Development: A key educational need is to develop the materials R&D workforce through cross-disciplinary training. Both junior and senior team members have led tutorials on concepts such as 3D printing, hyperuniformity, GitHub, and topological data analysis. We will submit a proposal to conduct a one-day Short Course at the American Physical Society (APS) March Meeting 2026, for which we will further develop these tutorials. We have shared our scientific progress at conferences (Materials Science and Technology, SIAM Materials Science). The Center for Advanced Manufacturing and Logistics (CAMAL) at NCSU has engaged the public through open-house demonstrations and the Raleigh SciTech Expo.

Data Management and Open Access: This work centers around a *configuration library* containing point-cloud data and adjacency matrices (.csv files) that describe the structures; it is accessible to all project team members through Globus. The unique identifier for each configuration tracks the point cloud to related configurations, STL files, physical 3D prints, and experimental data via a .xlsx database, with each physical sample having a QR code connected to its metadata in the database. The team has created a GitHub repository at https://github.com/DMREF-networks/ All repositories are currency private, and at the time of publications that reference these methods and data, they will be released to the public according to FAIR practices. We will make them **Findable** via hyperlinks in our talks, publications with DOIs, and websites; **Accessible** via public repositories in formats accessible to other researchers; **Interoperable** by providing necessary metadata and documentation to understand the files and file structures; and **Reusable** by establishing standard data formats with computer code to interconnect the elements.

Advancing Along the Materials Development Continuum and Partnerships to Translation: CAMAL is working with Freemelt, an electron beam AM manufacturer, to highlight our supportless metal printing. They provided a disordered metamaterials print demonstration at their booth during the RAPID 2024 conference.

Publications and References: There are no submitted manuscripts at this time.

Design of Superionic Conductors by Tuning Lattice Dynamics

Lead Investigator: Olivier Delaire (Duke University), olivier.delaire@duke.edu
Participating Institutions: Harvard University, Michigan State University, North Carolina State University
Source of Support: NSF-DMREF
Website: none
Keywords: ionic diffusion, lattice dynamics, thermodynamics, disorder, machine-learning

Project Scope

Superionic conductors (SICs) exhibit complex atomic dynamics, bridging extended time and length scales. Their thermodynamic and transport properties remain poorly understood, because of insufficient characterization of their atomic dynamics and the challenge to computationally access all relevant time/length scales. This project aims to achieve atomistic understanding of the interaction between mobile ion and framework dynamics, effects of entropy and frustration, as well as spatial and temporal correlations, to develop a predictive description for superionic behavior and accelerate the discovery of new SICs. Design hypotheses and model superionic compounds are shown in **Figure 1**.

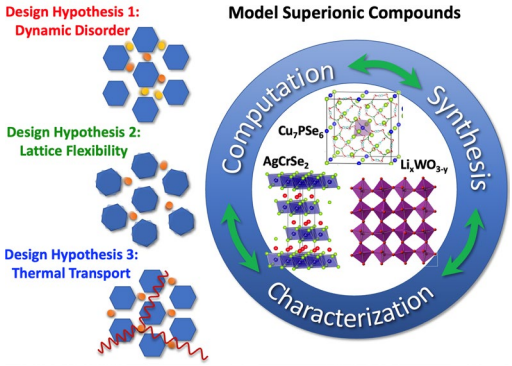


Figure 1. Design hypotheses and target superionic compounds.

Relevance to MGI

The primary goal of this project is the development of an integrated computational and experimental approach capable of predicting diffusive and thermal properties of SICs, and to ultimately discover new materials. Our interdisciplinary team explores three design hypotheses, as summarized in **Figure 1**, featuring iterative synergy between simulations, experiments, and identification of key physical phenomena. Many parameters have been correlated with superionicity: unit cell volume, size of the diffusion bottleneck, anion chemistry, topology of the anion sublattice, as well as microstructure. Yet, previously proposed descriptors mostly ignore the collective sublattice dynamics and flexibility of the framework, despite emerging evidence for their importance. The details of this connection remain largely unknown because of the scarcity of atomically resolved measurements to benchmark microscopic theories of superionicity, and because of computational challenges. The project addresses this gap through a comprehensive approach integrating novel computational infrastructure with synthesis and characterization at state-of-the-art facilities, which, combined, allow us to capture all the relevant atomic-scale processes underlying thermodynamic and transport phenomena. This will reveal and chart a path toward controlling the interplay of lattice flexibility and ionic correlations in fast ion diffusion. The new understanding will be encapsulated in chemical and structural rules and descriptors, applicable to the data-driven understanding and design of new superionic conductors.

Technical Progress

We use a multi-pronged approach fusing together state-of-the-art theoretical and experimental tools to build the fundamental knowledge base currently missing in SICs research. Our research approach utilizes several materials systems as platforms for testing the design hypotheses which includes mixed ion-electron conductors and systems whose composition is dynamic. We've made significant progress in understanding the atomic structure, dynamics, and superionic diffusion in layered chalcogenides $ACrX_2$. We synthesized a library of $ACrX_2$ (A = Ag, Cu; X = Se, S) and performed elastic, thermal and electronic transport measurements as well as quasi-elastic scattering, X-ray diffraction, and first-principles calculations. This comprehensive evaluation reveals important findings on the role of cation and anion substitution on the electrical, thermal, and ionic properties as a function of cation and anion substitution and temperature. For example, we found a systematic trend of overdamped low-energy phonons upon crossing into the superionic phase, giving rise to quasielastic response over a wide frequency range (several meV). Across the superionic phase transition, depending on the phonon eigenvector contributions of the mobile ions, the phonon modes selectively break down. We also probed the limited cation solubility regions within the Ag-Cu and Ag-Li systems from experiments and theory. We performed extensive neutron/X-ray scattering measurements on

other superionic compounds in the argyrodite family, such as Li_6PS_5Cl, $Li_{6P}S_5Br$, Ag_8SnSe_6, Ag_8GeS_6 (including single crystals of Ag_8GeS_6 and Ag_8SnS_6). These studies were extended into a computational investigation of the interface dynamics of Li-containing argyrodite compounds with Li metal. We further evaluated the lattice dynamics of transition metal oxide mixed ion conductors whose composition is tuned dynamically using electrochemical ion insertion, which is relevant for battery electrode materials. We characterized the lattice dynamics using operando atomic force microscopy and in situ X-ray diffraction. First-principles simulations were utilized to reveal the theoretical lattice expansions, energetic differences between different types of cation species, and MD simulations for their local mobilities. Finally, cross cutting computational work was used to develop ML methods for describing the potential energy surface computed with density functional theory to develop large and long-time MD simulations with ML models at near-quantum accuracy. This was applied to the study of superionic transport in solid-acid electrolytes.

Future Plans

Future work includes utilizing the combined experimental and computational tools to further expand the design criteria in the superionic conductors investigated thus far. For example, we are synthesizing mixed anion systems in the $ACrX_2$ family. Preliminary results of the phase transition temperature as a function of composition in the $CuCrSe_{2-x}S_x$ system show nonlinear behavior, suggesting that added configurational entropy helps to suppress the transition temperature. Importantly, the anion substitution appears to be possible over a broader composition range than cation substitution. In the case of the transition metal oxide mixed ion conductors, we've expanded the composition range beyond oxygen-deficient tungsten oxide to include multi-transition metal systems in the shear-phase oxide families. With these compositions, we can probe the influence of configurational entropy (as well as structure) on the lattice dynamics.

Broader Impacts and Workforce Development

The project supports the training of graduate and undergraduate students and postdoctoral fellows in interdisciplinary research at the interface of experiment and theory. To capitalize on the team's diverse expertise, we will hold annual 2-day hybrid workshops (in-person and virtual) organized by the PIs and their students. The workshops will be designed to introduce non-specialists to the expertise of each group. Co-PI Augustyn is the founder and faculty advisor of the SciBridge project at NC State, which develop experiment kits on renewable energy for partner universities in east Africa to further global engineering education. Co-PI Zevalkink is involved in K-12 outreach in mid-Michigan, encouraging K-12 girls to choose STEM by working with the Women in Engineering program at MSU. She has co-developed hands-on activities involving identification of single crystals from nature and the lab, deployed annually in engineering camps to reach ~200 students/year.

Data Management and Open Access

To automate calculations, collect and organize databases of results, we use AiiDA, a workflow automation and provenance-centered data management platform designed by Co-PI Kozinsky. We create tools for developing accelerated ML models, performing dynamics simulation and data analysis, emphasizing the reproducibility of the computed data as well as learned models and descriptors. Specifically, we will integrate the AIMD reference calculations, ML model training protocols and ML-MD trajectory generation and data analysis into workflows and release the computed data in the Materials Cloud repository.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Co-PI Kozinsky is a part-time principal scientist at BOSCH, coordinating the transfer of computational methods to industrial research efforts Plans are in place for BOSCH Research to adopt and apply computational methods that will be developed in this project.

Publications and References

1. M. Calderón-Cueva, E. Isotta, M. Rylko, B. Mukherjee, P. Scardi, A. Zevalkink, *Influence of Ge Lone Pairs on the Elasticity and Thermal Conductivity of GeSe–AgBiSe₂ Alloys*, Chem. Mater. **35**, 8984-8994 (2023). DOI: 10.1021/acs.chemmater.3c01616.
2. E. Isotta, W. Peng, A. Balodhi, A. Zevalkink, *Elastic moduli: a tool for understanding chemical bonding and thermal transport in thermoelectric materials*, Angew. Chem., **135**, e202213649 (2023). DOI: 10.1002/anie.202213649.

Synthetic machines from feedback-controlled active matter

Lead Investigator: Zvonimir Dogic
Participating Institutions: University of California at Santa Barbara and Brandeis University
Source of Support: NSF-DMREF
Website: none
Keywords: active matter, control, turbulence, self-shaping matter, autonomous dynamics

Project Scope

Active fluids exhibit persistent autonomous motion, an alluring life-like feature. However, on their own, they exhibit chaotic flows. Thus, they cannot perform functions such as generating work or driving net material transport. Using a combination of theory, experiment, and machine learning methods, we harness the chaotic dynamics of active fluids to achieve functional behaviors. We measure the instantaneous configuration of a light-responsive active fluid and use model-dependent theory and/or model-independent machine-learning methods to forecast its evolving dynamics. Using this information, we impose theory-guided external signals to close the feedback loop and steer the chaotic system toward a targeted dynamical state that is able to perform useful functions such as autonomous material transport.

Relevance to MGI

The MGI strategic plan seeks rapid development of new material functions through an iterative feedback loop between materials synthesis, experimental characterization, and theory/simulation. Such efforts require repeating cycles, in which theory guides materials synthesis and experimental characterization, which in turn provide new information to improve theories. Our project is inspired by biology where the cell is able to sense its environment and adjust its mechanical response in real time. We are developing light-responsive microtubule-based active fluids, active interface, and active liquid-liquid phase separation. These newly developed systems will allow for the implementation of envisioned iterative theory/experiment feedback cycles during a single experiment on a time scale of minutes. The cycle consists of the following steps: (1) experimentally measuring the instantaneous state of the system and extracting local structure and velocity fields, (2) use these measurements as an input into a theoretical or theory-independent machine learning framework to forecast the short-time system evolution, and (3) use the predictions from theory to adjust the external optical signal to change the local activity and steer the system toward a targeted functional state.

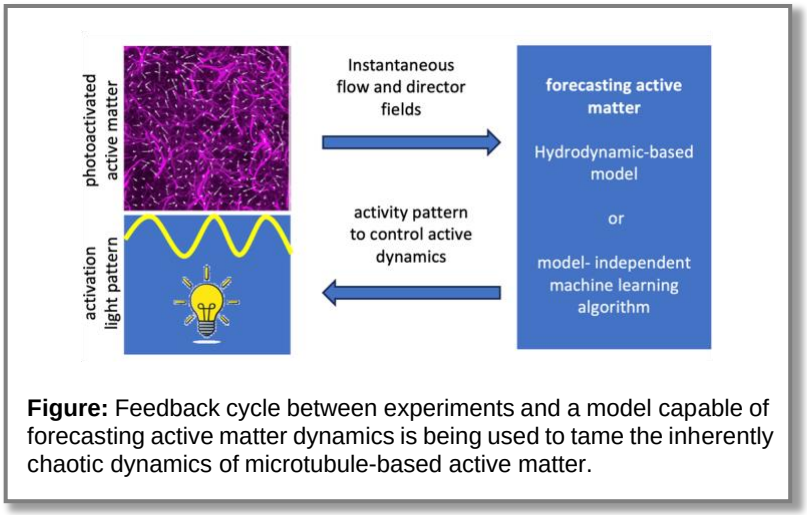


Figure: Feedback cycle between experiments and a model capable of forecasting active matter dynamics is being used to tame the inherently chaotic dynamics of microtubule-based active matter.

Technical Progress

We have completed several advances that are critical for implementing and developing the proposed closed-feedback loop for active matter samples. First, we have completed the development, purification, and characterization of light-responsive kinesin-molecular motors. These ATP-consuming nano-sized units are able to robustly power the chaotic dynamics of microtubule-based active fluids over a period of several hours. Second, using a high-resolution digital mirror device we have developed an optical microscope that is capable of projecting diascopic spatiotemporal illumination onto the sample. Importantly, the system is able to continuously project the illumination pattern over the entire centimeter-sized sample while allowing one to visualize any portion of the illuminated sample with a high magnification objective and epi-fluorescence imaging. Our efforts to simultaneously control the microscope stage, camera acquisition, and projected light pattern intensities in real-time were very glitchy using a conventional micro-manager-based environment. To overcome these obstacles, we are developing a pycro-manager-based protocol for controlling the

feedback cycle which should enable real-time operation. In a complementary direction, we are focusing our efforts on integrating our light-powered active fluids with active liquid-liquid phase separation created by a phase-separating polymer mixture of dextran and poly(ethylene glycol). In particular, we have developed modified surface treatment protocols that simultaneously allow us to systematically control the passive dextran/poly(ethylene glycol) interface from complete wetting to complete de-wetting and suppress the non-specific adsorption of all protein-based components of active fluids.

Future Plans

We have several near-term goals. First, our primary experimental focus is on integrating an optical microscope with a digital mirror device and real-time analysis code that would allow us to close the feedback loop. To test the performance of the system we will first perform classical proportional-integral-differential (PID) feedback to hold constant the average velocity of the active fluid. We will examine how various terms in the PID scheme affect the stability and variability of the chaotic systems. Second, we will explore how the system responds to patterns of activity that vary in both space and time. We will apply spatial patterns with different wavelengths and amplitudes. Third, with the recent arrival of the theory postdocs, we will focus on developing a comprehensive theoretical model that can quantitatively describe compressible isotropic active fluids and their response to applied spatiotemporal optical patterns. So far majority of models describe the behavior of active fluids in which the constituent density is spatially uniform. However, microtubule-based active fluids in the isotropic phase are highly compressible and as a result, we observed density buildup in the low-activity regions. This effect needs to be accounted for before we can predictably control active interface and active liquid-liquid phase separation. Once we accomplish the above-described near-term goals, we will initiate our work on controlling active interfaces and active liquid-liquid phase separation by spatial and temporal patterning of activity.

Broader Impacts and Workforce Development

The proposed research seamlessly merges experiments with theory, computation, and machine learning. It is an ideal platform for the interdisciplinary training of undergraduate and graduate students and postdoctoral fellows. The PIs are establishing a close and collaborative team where experimental and theoretical students continually interact with and learn from each other. All students receive extensive group and one-on-one mentoring focused on various aspects of planning research projects, analyzing experimental data, comparing theory and experiments, and presenting results for publications and presentations. Furthermore, UCSB is a Hispanic-serving institution with the largest physics undergraduate program in the country. We are committed to supervising undergraduate students in the DMREF-related research areas and thus steering them towards materials-science careers.

Data Management and Open Access

We are committed to expanding our practice to make all published experimental data, experimental and theoretical analysis, and simulation codes widely available and sharable on publicly accessible databases such as Dryad. We are also developing unique biological materials that are fairly intricate and challenging to prepare and purify. To lower the entry barrier for working on these systems to other laboratories we routinely host their members training them in sample preparation. We are also continuing the practice of providing biological materials to other groups.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We are focused on developing an entirely new category of dynamical, responsive, adaptive, and self-healing materials that can mimic the lifelike behaviors that have so far been mainly observed in living organisms. The key to these advances is controlling the inherently chaotic dynamics of microtubule-based active fluids. We are developing a unique experimental theoretical platform that allows a real-time intervention in controlling chaotic dynamics by applying patterns of active stresses that can vary in both space and time. The proposed research has the potential to elucidate universal principles for how to control chaotic dynamical systems thus turning their turbulent-like dynamics into materials that have well-defined functions.

Publications and References

DMREF: Collaborative Research: Computationally Driven Design of Tissue-Inspired Multifunctional Materials

PIs: Berkin Dortdivanlioglu, University of Texas at Austin, berkin@utexas.edu, Andy Sarles, University of Tennessee, Knoxville, ssarles@utk.edu, Robert Hickey, Pennsylvania State University, rjh64@psu.edu
Co-PI: Manish Kumar**,** University of Texas at Austin, manish.kumar@utexas.edu
Website: none.
Keywords: artificial tissues, biomimetic membranes, block copolymers, interface mechanics, 3D printing

Project Scope

Our objectives involve the computation-guided design, synthesis, characterization, and assembly of tissue-inspired materials made from cell-like polar compartments joined by biomimetic membranes. Using an integrated computational and experimental framework, our research studies the integration of self-assembling block copolymer microgels (BCP), biomimetic membranes (BMs), and stimuli-responsive biomolecules to form compartmentalized, tissue-like materials. Physics-based simulation tools based on multi-field continuum models enriched with interface mechanics are used to understand the collective mechanics of compartmentalized assemblies and build a machine learning (ML) model for enabling design exploration. We hypothesize that coupling hydrogel compartments through both mechanical (i.e., BCP cytoskeletons) and transport (i.e., selective BMs) mechanisms will lead to hierarchical, multifunctional tissues that match or exceed the performance of biological tissues.

Relevance to MGI

This work aims to fill a technical and practical gap in designing materials that approximate the spatially and temporally varied functionalities of cellularized biological tissues. The building blocks for this material architecture are based on a multiphase assembly of lipid-coated aqueous compartments (~10-100μm sized) in oil (Figure A). To overcome scale-up, deployment speed, and durability challenges, we devised an iterative feedback loop to link predictive physics-based simulations to experimental design and characterization with validations at various length scales. Trained on high-fidelity computations and experimental data, surrogate ML models are set to explore rapid designs that inform G-code instructions for 3D tissue-like printing and assembly. Given the vast design space across length scales and molecular constituents, the knowledge base created through our computationally driven experimental program is critical to elucidating key structural, mechanical, and transport-driven parameters needed to make rational choices to engineer materials that mimic structure-property relationships of biological tissues. This project combines expertise in computational modeling, machine learning, polymer synthesis and physics, biomembranes, protein channels, and 3D printing to synergistically develop hierarchical tissue-like materials that leverage cell-like compartmentalization, intercompartment communication via selective BMs, stimuli-responsiveness, and tunable mechanical properties.

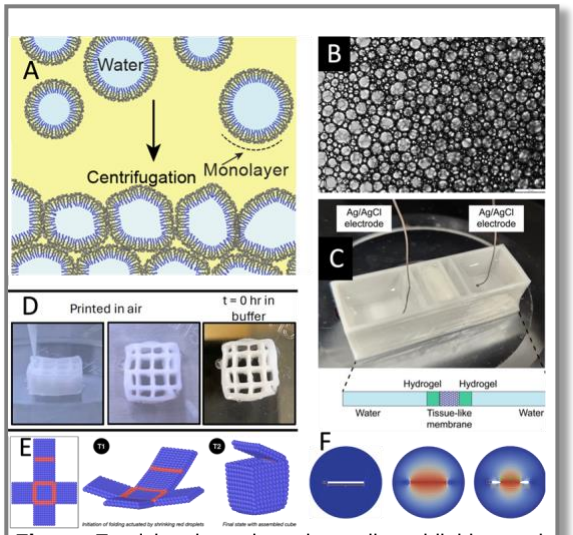


Figure. Emulsive tissue based on adhered lipid-coated polar compartments in oil. (A) Method to form emulsive tissue. (B) Brightfield image of tissue. (C) Membranes for electrically driven separation application. (D) 3D printed emulsive tissues in air (left) or aqueous buffer (right). (E) Folding droplet network simulation in LAMMPS. (F) Cohesive zone finite element method.

Technical Progress

In the past year, our team developed and studied a new approach for rapidly assembling lipid-stabilized hierarchical tissues, characterized polymeric BMs, and simulated through a dissipative particle dynamics framework, built on LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) that can handle very large systems of particles efficiently and allow mechanical and transport modeling of the interactions and behaviors at the mesoscale (See Figure). In parallel, we have also synthesized self-assembling BCP hydrogels and characterized their swelling and mechanical properties to demonstrate changing the relative fractions of the hydrophilic and hydrophobic moieties offers unique ways to tailor hydrogel properties, offering tunability of compartment stiffness.

Prior approaches (by us and others) to assemble lipid-stabilized tissues required the tedious and precise dispensing and positioning of discrete aqueous. As a milestone, we discovered that emulsifying the aqueous phase (e.g., vortexing) in a lipid-rich oil followed by centrifugation (Figure A) leads to a jammed assembly of lipid-coated aqueous compartments (Figure B) that can be used to build a functional tissue. This breakthrough has also been practically demonstrated in applications such as membranes for electrically driven separation (Figure C). The new approach is far easier, magnitudes of orders faster, and more scalable (mm-cm scale), features previously unattainable. To this end, the jammed assembly of membrane-stabilized compartments can be readily 3D printed in air or water to form intricate, multi-layer tissue geometries that are stable for hours to days (Figure D). Enriching the membranes with carriers or channels enables transport of species down a concentration gradient or along the path of an applied electric field. Our team used this capability to show that multi-layer emulsive tissues can effectively separate ions contained in adjacent reservoirs (Figure C). Rheological testing of the gels revealed an adhesive jammed network behavior with self-healing. Towards understanding these experiments, the adhesive failure and self-healing of bilayer interfaces are captured through a new cohesive zone finite element model (Figure F) adopting Lennard-Jones type pair-potential, revealing the role of geometric and material properties of compartments and membranes.

Future Plans

Through further improvement of our new 3D fabrication technique and targeted predictive models, future plans include developing actuating tissue-like materials to facilitate dynamic shape changes, incorporate stimuli-responsive channels/proteins into the BMs and within the compartments to add specific functionalities, towards actuation, chemical energy conversion, and drug release, and tune the mechanical properties of the emulsions. To this end, we will explore solidification of tissue-like materials by incorporating hydrogels within the compartments and using cross-linked (or cross-linkable) BCPs to covalently attached neighboring compartments. The enabled fabrication of large-scale tissue assemblies quickly leads to the creation of complex droplet systems, expected to generate abundant data. Computer vision techniques and neural networks suitable for image analysis will be developed to digitize this data, making it ready for the simulations via developed computational models.

Broader Impacts and Workforce Development

The project fosters cross-disciplinary exchanges and offers unique educational opportunities in the fundamentals of materials science, biophysics, mechanics, and computational sciences, as well as in engineering new tissue-inspired multifunctional materials. This project is serving to train 6 PhD and 5 undergraduate students from different disciplines at the 3 institutions. In addition to our regular online team meetings, several team members traveled to other campuses for in-person meetings, fostering deeper engagement.

Data Management and Open Access

The project has generated 11 journal papers and 12 conference presentations, 2 GitHub repository with an open-sourced software code. Works are in progress, committed to FAIR data practices, to share micromechanical characterization of hydrogel droplets and benchmark dataset for meta-models for folding droplet networks.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Our materials platform, enhanced by our recent discovery of scalable fabrication, addresses the knowledge gaps along the Materials Development Continuum to design modular, large-scale macroscopic materials. We are also making progress towards 3D printing in air, scaffold material, and liquid environments. Our project has the potential to provide a new class of materials that are both scalable and quick to deploy.

Selected Publications and References

1. S. Koner, J. Tawfik, F. Mashali, K. B. Kennison, W. T. McClintic, F. A. Heberle, Y.-M. Tu, M. Kumar, S. A. Sarles, Biochimica et Biophysica Acta-Biomembranes, 1864:183997, https://doi.org/10.1016/j.bbamem.2022.183997 (2022).
2. C. Lang, E. C. Lloyd, K. E. Matuszewski, Y. Xu, V. Ganesan, R. Huang, M. Kumar, and R. J. Hickey, Nature Nanotechnology, 17:752–758, https://doi.org/10.1038/s41565-022-01133-0 (2022).
3. A. Javili and B. Dortdivanlioglu, European Journal of Mechanics-A / Solids, 100:104981, https://doi.org/10.1016/j.euromechsol.2023.104981 (2023).
4. P. Giolando, and S. Kakaletsis, and X. Zhang, and J. Weickenmeier, and E. Castillo, and B. Dortdivanlioglu, and M Rausch, Soft Matter, 19:6710-6720, https://doi.org/10.1039/D3SM00402C (2023).

Simulation-informed models for amorphous metal additive manufacturing

Lead Investigators: Michael L. Falk mfalk@jhu.edu, Katharine M. Flores floresk@wustl.edu, Chris H. Rycroft rycroft@wisc.edu, Michael D. Shields michael.shields@jhu.edu, Paul M. Voyles voyles@engr.wisc.edu
Participating Institutions: Johns Hopkins Univ.; Univ. of Wisconsin, Madison; Washington Univ., St. Louis
Source of Support: NSF-DMREF 2323718/2323719/2323720
Website: none
Keywords: additive manufacturing, metallic glass, laser deposition, nano-diffraction, mechanical properties

Project Scope

This project aims to develop the underlying materials science and computational tools for the design of additively manufactured amorphous metals with desired mechanical properties. Amorphous metals, also termed metallic glasses have potential as a transformative material for additive manufacturing applications. Metallic glasses solidify without crystal structure promising superior structural homogeneity; laser processing can potentially overcome cooling-rate limitations for casting larger MG structures. Simulation-informed modeling is a first step toward a simultaneous design approach to achieve desired materials properties and performance.

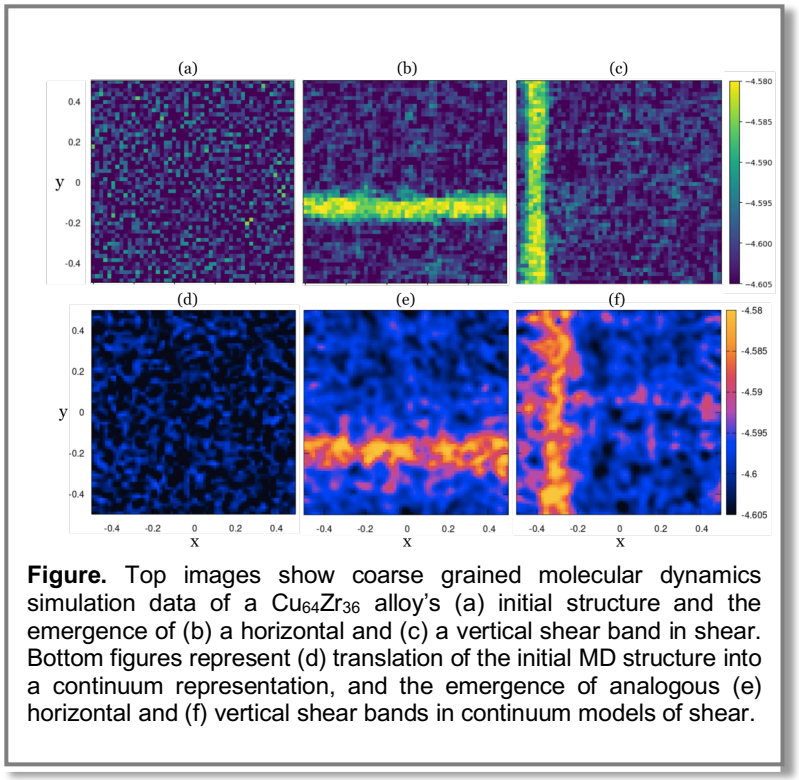


Figure. Top images show coarse grained molecular dynamics simulation data of a $Cu_{64}Zr_{36}$ alloy's (a) initial structure and the emergence of (b) a horizontal and (c) a vertical shear band in shear. Bottom figures represent (d) translation of the initial MD structure into a continuum representation, and the emergence of analogous (e) horizontal and (f) vertical shear bands in continuum models of shear.

Relevance to MGI

The research seeks to develop a virtual cycle between MG processing by direct laser deposition and high-fidelity physical models. Machine learning (ML) is used to quantify key order parameters from nanometer-resolution electron nano-diffraction and atomistic simulation data, relating experimental and simulation data. Based upon these inputs continuum numerical tools predict how processing gives rise to the strength and toughness of the resulting materials. The underlying models are based on simulation-derived data from atomic-scale simulation. Validation will be achieved by direct comparison to *ex situ* and *in situ* mechanical testing. Uncertainty quantification will be included in these models *a priori*.

The proposed research supports the Materials Genome Initiative by: (1) Identifying structural order parameters for mechanical properties of metallic glasses from experiments and simulations using machine learning. (2) Incorporating these order parameters and their evolution with thermal history and strain into predictive models of metallic glass mechanical properties including strength and toughness. (3) Developing simulation-informed models that combine additive manufacturing processing and mechanical property prediction. This work will lay the scientific groundwork for computational design tools for additive manufacturing of amorphous metals.

Technical Progress

We have completed the formulation of our initial simulation-data-informed models, which we term a Stochastic Evolution Elastoplastic Model (SEEM), into our continuum formulation. Our investigations this year revealed the importance of capturing nonlinear elastic effects in the SEEM. The preliminary results are shown in Figure 1. We have submitted a first publication regarding the SEEM framework that highlights its capacity to emulate the predictions of atomistic simulations with considerably less computational effort [1]. A follow-on publication regarding the continuum integration of the SEEM model is in preparation. Considerable work has been completed applying nano-diffraction analysis to simulated metallic glass structures. To build a machine learning framework capable of characterizing relevant structural order parameters from these nano-diffraction images, a variational auto-encoder is now being constructed to differentiate these images. Our initial effort focuses on distinguishing rapidly and more slowly quenched glasses from their nano-diffraction signatures. Initial laser deposition studies and have been undertaken with elemental powders that were immediately available. These have successfully produced samples, but characterization studies have revealed incorporated oxide in our final parts.

Future Plans

We are working to obtain pre-alloyed powder that will result in high purity laser deposits more suitable for comparison with the models. In the meantime, we are working toward characterizing as-cast materials. Nano-diffraction studies from these samples will be compared with data derived from simulations. This will test our capacity to utilize machine learning tools derived from simulated to data to quantify real material. We are also initiating the development of process models that will provide spatially resolved predictions of variation in metallic glass structures in as-deposited parts. This effort will start with remelted dots and proceed to more complex structures. In future years mechanical property prediction from modeling tools based on these results will be tested experimentally to validate our simulation tools.

Broader Impacts and Workforce Development

We are engaging students, postdoctoral researchers, and faculty across three universities in a learning community within which we will create and pilot pedagogical materials that support graduate student professional development in online communication. This effort will build on the PIs' experiences developing online content for courses (All), public communication (Rycroft, Voyles), MOOCs (Shields), and to serve outreach programs for underserved communities (Falk, Flores). The pedagogical modules developed will teach how to effectively engage diverse audiences of various ages considering both students and the broader community. We have so far engaged the students and postdocs in the selection of projects to be undertaken over the next several months. These include:

- short-form videos to explain aspects of the materials science of metallic glasses,
- pedagogical materials regarding materials simulation, mathematical modeling, and programming, and
- introductory videos regarding computer-aided-design for 3D printing.

Data Management and Open Access

We have requested space within the Johns Hopkins Research Data Repository with a DOI for the dataset associated with our first publication. This data will be uploaded shortly and made publicly available.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Additive manufacturing of amorphous metals is a potentially transformative technology. It is currently limited to small scale and specialty parts. The proposed work will advance toward more general application. As a result, this project supports national priorities in advanced manufacturing technology at the intersection with mathematical methods and data science.

Publications and References

1. B. Xu, Z. Wu, J. Lu, M.D. Shields, C.H. Rycroft, F. Bamer, M.L. Falk, *Stochastic evolution elasto-plastic modeling of a metallic glass*, 2024 (submitted).

Systematic discovery of materials platforms for spin-light quantum interfaces

Lead Investigator: Michael E. Flatté, michaelflatte@quantumsci.net
Participating Institutions: U. Iowa (MEF), Brown U. (Rashid Zia), U. Pennsylvania (PI Lee C. Bassett)
Source of Support: NSF-DMREF 1922278, 1921877, 1922025
Website: none
Keywords: spin-photon interfaces, crystal-field splitting, spin dynamics.

Project Scope

To accelerate the discovery of defects, dopants, and host materials optimized for quantum information science. The project is organized in three thrusts: (1) prediction of new defects, (2) systematic discovery and efficient characterization, and (3) refinement, generalization and in-depth study of new defects. The project's research goals are coupled with a mission to educate students and the public about quantum information science, and to generate open-source resources for the scientific community.

Relevance to MGI

Quantum information science and engineering (QISE) merges multiple disciplines including physics, chemistry, materials science, optics and electrical engineering. The rapidly expanding QISE field is motivated by potential applications to important issues including secure communication, navigation, machine learning, optimization, and simulations of complex materials systems. Throughout the history of QISE research, the discovery and development of new material platforms has facilitated transformational advances in our understanding of fundamental principles of quantum coherence and control, and ultimately led to devices with superior performance for QISE applications.

In this project we have combined experimental measurements of spinful defects with advances in the calculation of crystal field parameters for defects and fine structure splittings. Furthermore we have developed a powerful tool for simulating optically-detected magnetic resonance (ODMR) and used this to classify the defects emerging from measurements in several materials (SiC, hBN).

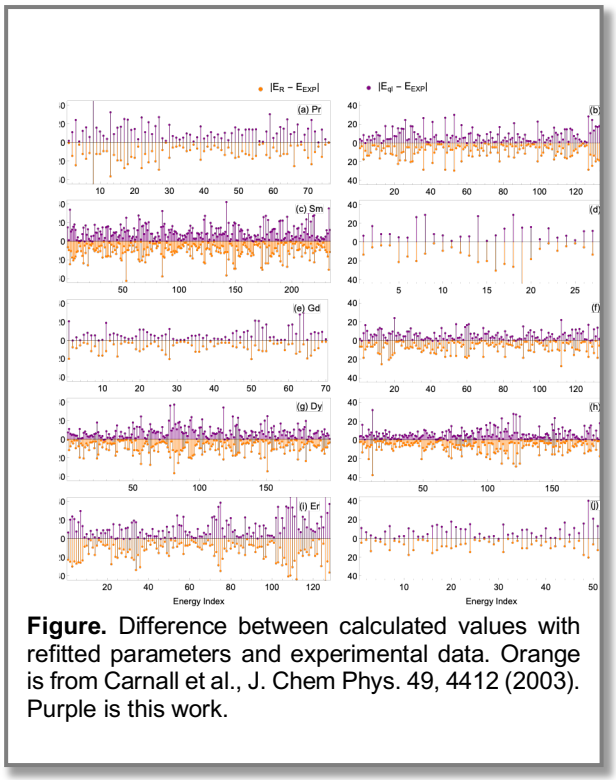


Figure. Difference between calculated values with refitted parameters and experimental data. Orange is from Carnall et al., J. Chem Phys. 49, 4412 (2003). Purple is this work.

Technical Progress

Research has addressed all three scientific goals of the project, with an emphasis on prediction and efficient characterization of new defects. These include:

Prediction: First principles calculations of transition-metal complexes in ZnS, estimated fine structure of transition-metal impurities, first principles calculations of lanthanides in Y_2O_3 and other hosts, and predicting fine structure for lanthanide impurities.

Systematic discovery and efficient characterization: Efficient, automated characterization of quantum emitters, photoluminescence excitation spectroscopy and resonant excitation of defects, systematic characterization of implanted impurities, combinatorial search of defect-host structures, and identification and characterization of single emitters in PL microscopy.

Refinement, generalization and in-depth study: Calculations of Cu-V complexes in ZnS, synthesis and characterization of Cu-doped colloidal ZnS, single-particle spectroscopy of Cu-doped ZnS nanoparticles, optical dynamics of single defects in h-BN, and detailed fitting of the crystal field splittings in lanthanides using full free-ion terms.

Three highlights from this past year are: (1) prediction of fine structure cancellation in highly asymmetric quantum dots, (2) resolution of literature database errors and new simulations of crystal field splittings and emission intensities of lanthanides in hosts, and (3) identification of a room-temperature-stable spinful defect demonstrating ODMR in hBN.

The fine structure calculations have been implemented for any spin-1 defect, but were applied to studies of InAs/InP quantum dots and showed that different contributions to the exchange interaction can cancel for asymmetric dots, indicating that it is not necessary to have a highly symmetric quantum dot for fine structure splitting cancellation (thus enabling biexciton cascade for entangled photon pair emission).

For the past couple decades the tables of *Carnall et al.* J. Chem Phys. 49, 4412 (2003) have been used for understanding crystal field splittings of lanthanides in various hosts. The crystal field splitting parameters were obtained with various approximations that simplified the complex strongly-correlated physics of the 4f host. By going beyond these approximations, and correcting errors in the tables, we have sorted out this database for the community.

The search for a room-temperature spinful defect in hBN has been motivated by interest in quantum sensing using materials less expensive and easier to obtain than diamond. We have characterized such a defect and described the transition dynamics using an efficient constrained search for parameters in the ODMR simulation. This builds on our work to be submitted soon on ODMR on the silicon vacancy in SiC hosts.

In addition there have been activities in outreach and education, including teaching quantum engineering, outreach to K-12 students and the public, and engagement with the scientific community.

Future Plans

This project is concluding soon, and therefore our goals will be to package the materials (i.e. *qlanth*, which simulates crystal field splittings for rare-earth dopants; *magres*, our ODMR simulation tools) for the community.

Broader Impacts and Workforce Development

Our team's scientific research has been coupled with a broad educational mission to educate students and the general public about materials science and the emerging field of QISE. This collaborative project engages both undergraduate and graduate students, with an emphasis on recruiting and supporting women and other historically underrepresented groups. Of the team who worked on the project this year, four are women and two are Latino. The junior researchers contributing to the figure presented on page 1 were both Latino. All team members benefitted from the opportunity to participate in a transdisciplinary, multi-institutional collaboration, where they gain access to computational and experimental resources as well as expertise that benefits their research.

Data Management and Open Access

Data is being made available online in a publicly accessible fashion. We are preparing qlanth (github.com/qlanth) for public release as we complete our testing and finalize our submitted paper. Data from our published papers is available in full in supplementary material and, where necessary in addition, public repositories. For example, for the PRX Quantum volume 4 article, (https://github.com/penn-qel/photon-emission-correlation-spectroscopy).

Advancing Along the Materials Development Continuum and Partnerships to Translation

QISE is an area of unprecedented growth as well as substantial applied funding. Although there are fundamental limits to the spin-photon interfaces currently explored there is still progress at a rate that VC's find acceptable. Hence the tolerance for risk in the applied community is relatively low for new materials. We anticipate that as some current approaches plateau the interest from the applied community in these new materials will rapidly increase.

Publications and References

1. R. N. Patel, R. E. K. Fishman, T.-Y. Huang, J. A. Gusdorff, D. A. Fehr, D. A. Hopper, S. A. Breitweiser, B. Porat, M. E. Flatté, L. C. Bassett, "Room Temperature Dynamics of an Optically Addressable Single Spin in Hexagonal Boron Nitride", Nano Lett. 24, 7623-7628 (2024). DOI: 10.1021/acs.nanolett.4c01333
2. N. R. S. van Venrooij, A. R. da Cruz, R. S. R. Gajjela, P. M. Koenraad, C. E. Pryor, and M. E. Flatté, "Fine structure splitting cancellation in highly asymmetry InAs/InP droplet epitaxy quantum dots", Physical Review B 109, L201405 (2024). DOI: 10.1103/PhysRevB.109.L201405
3. A. Gali, A. Schleife, A. J. Heinrich, A. Laucht, B. Schuler, C. Chakraborty, C. P. Anderson, C. Déprez, J. McCallum, L. C. Bassett, M. Friesen, M. E. Flatté, P. Maurer, S. N. Coppersmith, T. Zhong, V. Begum-Hudde, and Y. Ping, "Challenges in advancing our understanding of atomic-like quantum systems: Theory and experiment" MRS Bulletin 49, 256-276 (2024). DOI: 10.1557/s43577-023-00659-5
4. S. M. Thompson, C. Sahin, S. Yang, M. E. Flatté, C. B. Murray, L. C. Bassett, and C. R. Kagan, "Red Emission from Copper-Vacancy Color Centers in Zinc Sulfide Colloidal Nanocrystals", ACS Nano 17, 5963-5973 (2023). DOI: 10.1021/acsnano.3c00191
5. C. Bhandari, C. Sahin, D. Paudyal, and M. E. Flatté, "Distinguishing erbium dopants in Y_2O_3 by site symmetry: ab initio theory of two spin-photon interfaces", Physical Review Materials 7, 126201 (2023). DOI: 10.1103/PhysRevMaterials.7.126201
6. R. E. K. Fishman, R. N. Patel, D. A. Hopper, T.-Y. Huang, and L. C. Bassett, "Photon-Emission-Correlation Spectroscopy as an Analytical Tool for Solid-State Quantum Defects", PRX Quantum 4, 010202 (2023). DOI: 10.1103/PRXQuantum.4.010202
7. R. N. Patel, D. A. Hopper, J. A. Gusdorff, M. E. Turiansky, T.-Y. Huang, R.E.K. Fishman, B. Porat, C. G. Van de Walle and L. C. Bassett, "Probing the Optical Dynamics of Quantum Emitters in Hexagonal Boron Nitride", PRX Quantum 3, 030331 (2022). DOI: 10.1103/PRXQuantum.3.030331
8. L. R. Narun, R. E. K. Fishman, H. J. Shulevitz, R. N. Patel, and L. C. Bassett, "Efficient Analysis of Photoluminescence Images for the Classification of Single-Photon Emitters", ACS Photonics 9, 3540-3549 (2022). DOI: 10.1021/acsphotonics.2c00795
9. C. Bhandari, M. E. Flatté, D. Paudyal, "Enhanced magnetic anisotropy in lanthanum M-type hexaferrites by quantum-confined charge transfer", Physical Review Materials 5, 094415 (2021) DOI: 10.1103/PhysRevMaterials.5.094415

Designing Optical Materials with Small-Molecule Ionic Isolation Lattices (SMILES)

Lead Investigator: Amar H Flood, aflood@indiana.edu
Participating Institutions: Indiana University, Georgia Institute of Technology
Source of Support: NSF-DMREF
Website: https://smiles.iu.edu/
Keywords: optical, upconversion, fluorescence, molecular materials, crystals

Project Scope: We created the brightest optical materials called SMILES (small-molecule, ionic isolation lattices, ***Figure 1***).[1] The team involves theory (Krishnan Raghavachari), data (Sudhakar Pamidighantam) and experiment (Amar Flood), and collaborators in the US and the globe, and in industry.

We are developing data tools to create and mine databases to select dyes for making SMILES materials, developing efficient methods to simulate optical properties, learning crystal engineering and structure-property relationships to create functional materials spanning crystals, films, nanoparticles, and polymer systems imbued with specific optical properties. We will accelerate creation of materials with advanced optical properties for emission of white, chiral, and upconverted light with potential use in displays, solar energy and bioimaging.

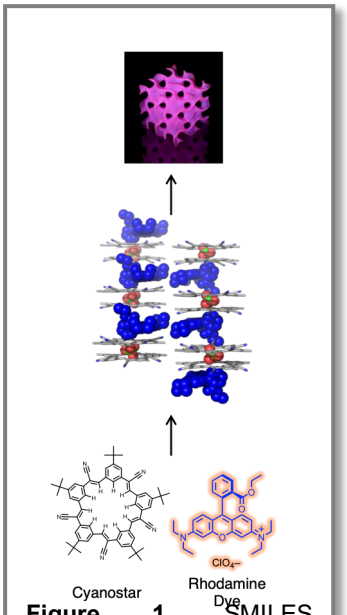


Figure 1. SMILES materials are made by mixing cyanostar (left) with dyes (right) to form crystals (middle) that can be processed into materials (top) for generating optical properties by design

Relevance to MGI: We achieve tight integration using a design loop involving all team members. We delineate the target optical property and develop the design rules for the properties needed in the building blocks to manipulate light and crystal packing. We use data mining, computation and retrosynthesis to identify dyes with desired properties. The dyes are synthesized, crystallized as SMILES, the crystal structure and optical materials characterized to establish structure-property relationships. Use of data, theory and synthesis in the design accelerates materials creation and understanding. Our papers integrate theory, synthesis, and characterization. Thus, each component interacts to push advances in each other. E.g., new databases, electronic structure calculations, synthesis, growth and crystal engineering rules and methods are being developed.

To accelerate discovery, we remove bottlenecks in the design loop by conducting fundamental research, e.g., we created a dye database by developing methods to mine the literature. We also conduct studies to test hypotheses underpinning performance of SMILES materials. E.g., exploration of crystal engineering led to the brightest fluorescent nanoparticles in 2 years;[2] 10x faster than current attempts.

Technical Progress: To accelerate design, we established a series of simulations, data mining tools and schema.[3] We tested Δ-SCF methods to predict emission maxima of large dye molecules for use in SMILES.[4] Using 12,318 dye-solvent combinations, the initial maximum overlap method (IMOM) results are faster and as accurate as TD-DFT at predicting the S_1 excited state and emission maxima with a mean absolute error of 0.27 eV, further reducing to 0.17 eV using calibrations by dye class. We also extracted and analysed redox and optical data[5] in the literature on dyes for creating SMILES using three design rules: The dye needs (1) a positive charge, (2) an aligned redox window, and (3) to be smaller than 2 nm. We analyzed a database of 20,000 entries augmented with the literature. We found 57 dyes to be compliant with the SMILES design rules (***Figure 2***). Due to problems with reported electrochemical data, we are instead using DFT to calculate electrochemistry for data mining and the design loop.

We tested and found evidence for the design rule that the dye needs to be smaller than 2 nm to produce emissive materials. We also examined NIR emission at 700-900 nm. The NIR SMILES nanoparticles were used for in-vivo tumor imaging of mice bearing human xenograft tumors by exploiting the EPR effect and are promising for bioimaging applications.[6] We conducted fundamental studies of energy transfer[7] that contributes to the brightness and, by leveraging FRET, can be used for enhancing brightness and controlling the fluorescent lifetimes of materials[8] and nanoparticles for FLIM imaging.[9]

Towards materials with advanced functions, we made ultra-bright materials and nanoparticles that display circularly polarized luminescence (CPL) using chiral dyes.[10] We used a multi-disciplinary effort combining synthesis, materials creation, theory and characterization. The SMILES concept allowed us to accelerate development of CPL materials. Towards solid-state upconversion, we used theory and characterization to determine the triplet energy of the cyanostar complex at 2.0 eV,[11] needed in the design of sensitizer and annihilator dyes.

We have undertaken multi-disciplinary research with physicists at CUNY showing use of SMILES as new polariton materials.[12] Using a 35-nm polymer-SMILES film inside optical cavities of devices that function as lasers, we also showed formation of Bose-Einstein-like condensates, enabling top-down fabrication of a room-temperature polariton condensate lattice.[13] In a new application with analytical chemist (Goda) at Tokyo University we used the SMILES concept to improve the limits of detection of Raman-based probes with potential use in cancer detection.[14]

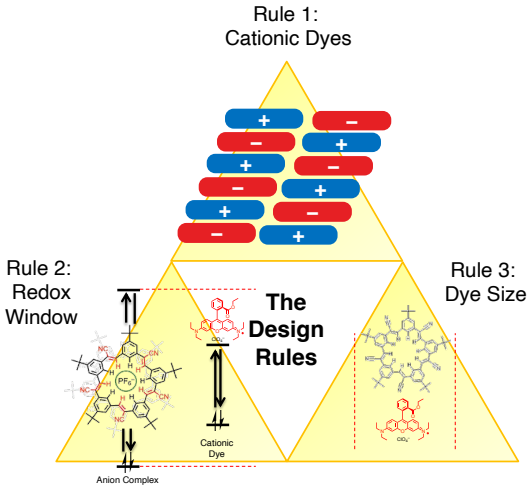


Figure 2 The 3 design rules used to generate a collection of 57 SMILES-compliant dyes from 20,000 candidates, and to develop SMILES materials displaying CPL, and the basis for upconversion materials

Future Plans: We will implement the design workflow on our SMILES Gateway to allow mining, design and generative AI approaches to identifying dye candidates for making fluorescent SMILES materials of any color and lifetime, for use in blue emission, optimized CPL, and for use in upconversion materials. We are exploring the crystal engineering rules at a fundamental level, e.g., to make SMILES with dye dimers for upconversion. Ultimately, the goal is to provide the design framework to accelerate the creation of functional materials, and to demonstrate this capability with upconversion.

Broader Impacts and Workforce Development: Project goals and MGI philosophy are being conveyed using talks (10), posters (5), one-on-one meetings (75), informal conversations, our website (SMILES.iu.edu) and access to the MRS-TV coverage on YouTube, reaching 600+ people. We provided outreach opportunities at Indiana University's Science Fest in Spring 2024, impacting 300+ K-12 students. Our presentations emphasize the design loop of materials creation, use of data mining and quantum calculations, to direct synthesis and the role of feedback from characterization to refine fundamental rules of SMILES materials creation. We have hosted 4 high school students during summer of 2023 for hands-on experience making SMILES materials.

We collaborate with Bo Laursen and Junsheng Chen (Uni Copenhagen), Jerome Lacour (Uni Geneva), Bo Albinsson (Chalmers Uni), K. Goda (Uni Tokyo), Vinod Menon (CUNY) and Matt Sfeir (ASRC).

Data Management and Open Access: The SMILES databases and database schema are being implemented on the SMILES gateway (https://gateway.smiles.iu.edu/) and will be in a searchable format and accessible to authorized users through the SMILES gateway. SMILES data will be periodically released. We plan to release an API for external users. We plan to release computational data into PubChemQC and the QC Archive for community access and X-ray crystal structure data in FAIR compliant format into the Cambridge Structure Database.

Advancing Along the Materials Development Continuum and Partnerships to Translation: We are engaged in a collaboration with start-up, Halophore, Inc., to commercialize SMILES technology. We are also initiating a collaboration with Scifinder® on extracting electrochemistry data from the literature. The SMILES Gateway will be part of an open-source and open-access portal for SMILES materials design.

The original SMILES patent[15] is currently being examined in US, Japan, Korea and China. A new patent has been filed on the polariton lasers.[16]

We are also exploring new commercialization opportunities with a regional ICORPS for nanoparticle bioimaging. Graduate student, Andrew Olsson, is the entrepreneurial lead, PI Flood is the technical lead, and Halophore CEO, Chris Benson, is the business lead. We are also planning to apply to the PFI program and are using the outcomes of the ICORPS to shape the business case.

List of Publications and Patent Activity

1 Benson, C. R.; Kacenauskaite, L.; VanDenburgh, K. L.; Zhao, W.; Qiao, B.; Sadhukhan, T.; Pink, M.; Chen, J.; Borgi, S.; Chen, C.; Davis, B. J.; Simon, Y. C.; Raghavachari, K.; Laursen, B. W.; Flood, A. H., Plug-and-play Optical Materials from Fluorescent Dyes and Macrocycles, *Chem* **2020**, 6, 1978-1997. (Primary work, published prior to current grant but supported from the DMREF program) https://doi.org/10.1016/j.chempr.2020.06.029

2 Chen, J.; Ali Fateminia, S. M.; Kacenauskaite, L.; Bærentsen, N.; Stenspil, S. G.; Bredehoeft, J.; Martinez, K. L.; Flood, A. H.; Laursen, B. W., Ultra-Bright Fluorescent Organic Nanoparticles Based on Small-Molecule Ionic Isolation Lattices, *Angew. Chem. Int. Ed.*, **2021**, *60*, 9450. (Primary work, published prior to current grant) https://doi.org/10.1002/anie.202100950

3 Sudhakar Pamidighantam, Lahiru Jayathilake, Yu Luo, Xingyi Zhou, Marcus Christie, Michaela Loveless, Amar H. Flood, Data infrastructure for Small Molecule Ionic Isolation Lattice Materials. *PEARC 24*, *under review*

4 V. Tripathy, A. H. Flood, K. Raghavachari, Accelerated computer-aided screening of optical materials: Investigating the potential of Δ-SCF Methods to predict emission maxima of large dye molecules, *J. Phys. Chem. A.* accepted

5 Loveless, M. K.; Che, M.; Sanchez, A. J.; Tripathy, V.; Laursen, B. W.; Pamidighantam, S.; Raghavachari, K.; Flood, A. H., Extracting Recalcitrant Redox Data on Fluorophores to Pair with Optical Data for Predicting Small-Molecule, Ionic Isolation Lattices, *Digital Discovery*, *under review*

6 NIR: Near-Infrared Emitting Organic Nanoparticles Based on Small-Molecule Ionic Isolation Lattices for in-vivo Imaging of Human Brain Cancer, Junsheng Chen, Karina Juhl, Yanmei He, Amar H. Flood, Andreas Kjaer, Bo W. Laursen *ACS Materials Letters*, under review

7 Chen, J.; Stenspil, S. G.; Kaziannis, S.; Kacenauskaite, L.; Lenngren, N.; Kloz, M.; Flood, A. H.; Laursen, B. W., Quantitative Energy Transfer in Organic Nanoparticles Based on Small-Molecule Ionic Isolation Lattices for UV Light Harvesting, *ACS Appl. Nano Mater.* **2022**, 5, 13887-13893. https://doi.org/10.1021/acsanm.2c018999

8 Kacenauskaite, L.; Olsson, A. H.; Flood, A. H.; Laursen, B. W., Universal Concept for Bright, Organic, Solid-State Emitters-Doping of Small-Molecule Ionic Isolation Lattices with FRET, *J. Am. Chem Soc.* **2022**, *144*, 19981-19989. https://doi.org/10.1021/jacs.2c08540

9 Stenspil, S. G.; Chen, J.; Liisberg, M. B.; Flood, A. H.; Laursen, B. W., Control of the fluorescence lifetime in dye based nanoparticles, *Chem. Sci.* **2024**, *Advance article* https://doi.org/10.1039/D3SC05496A

10 Stine G. Stenspil, Andrew H. Olsson, Rebecca Mucci, Maren Pink, Céline Besnard, Jérôme Lacour, Amar H. Flood and Bo W. Laursen, Supramolecular Control of Helicene CPL Emitters in Molecular Solids and Bright Nanoparticles, *Angew. Chem. Int. Ed.* submitted

11 Edhborg, F.; Olesund, A.; Tripathy, V.; Wang, Y.; Sadhukhan, T.; Olsson, A. H.; Bisballe, N.; Raghavachari, K.; Laursen, B. W.; Albinsson, B.; Flood, A. H., Triplet States of Cyanostar and its Anion Complexes, *J. Phys. Chem. A*, **2023**, *127*, 5841-5850. https://doi.org/10.1021/acs.jpca.3c02701

12 Deshmukh, P.; Satapathy, S.; Michail, E.; Olsson, A. H.; Bushati, R.; Yadav, R. K.; Khatonair, M.; Chen, J.; John, G.; Laursen, B. W.; Flood, A. H.; Sfeir, M. Y.; Menon, V. M., Plug-and-play molecular approach for room temperature polariton condensation, *ACS Photonics*, **2024**, *11*, 348-355 https://doi.org/10.1021/acsphotonics.3c01547

13 Yadav, R. K.; Satapathy, S.; Deshmukh, P.; Datta, B.; Sharma, A.; Olsson, A. H.; Chen, J.; Laursen, B. W.; Flood, A. H.; Sfeir, M. Y.; Menon V. M., Direct writing of room temperature polariton condensate lattice *Nano Letters*, **2024**, *online* https://doi.org/10.1021/acs.nanolett.4c00586

14 Nishiyama,R. Furuya, K.; McCann, P.; Kacenauskaite, L.; Laursen, B. W.; Flood, A. H.; Hiramatsu, K.; Goda, K. Boosting the Brightness of Raman Tags Using Cyanostar Macrocycles, *Anal. Chem.* **2023**, *online* https://doi.org/10.1021/acs.analchem.3c01958

15 ***US Patent Application:*** Flood, A. H., Laursen, B. W. Color matched and bright fluorescent materials composed of small-molecule ionic lattices (Filing Date: March 10, 2019; U.S. Provisional App. No. 62/641,281)

16 ***US Patent Application and PCT:*** Flood, A. H., Yadav, R.; Satapathy, S.; Deshmukh, P.; Menon, V.; Laursen, B., Room temperature polariton condensation (Filing Date: Aug 7, 2023; PCT/US2023/029619)

Machine Learning Quantum Monte Carlo Energies and Charge Densities using Graph Neural Networks

Lead Investigator: Panchapakesan Ganesh, ganeshp@ornl.gov (Center Director, Paul Kent, kentpr@ornl.gov)
Participating Institutions: Oak Ridge National Laboratory, Brown University, Georgia Institute of Technology
Source of Support: DOE-BES
Website: https://cpsfm.ornl.gov
Keywords: Quantum Monte Carlo, machine learning, charge density, many-body energy, graph neural networks

Project Scope
To increase the impact of high accuracy Quantum Monte Carlo (QMC) data, we are developing workflows to perform systematic studies of molecules and materials and obtain more data than the traditional one at a time QMC approach. (i) In condensed matter systems, data from workflows for studies of bilayers of 2D materials (BN, MoS_2, WTe_2, etc.) provide insight into the van der Waals interactions and charge transfer in heterostructures that can result in novel behavior, as well as inform other theory approaches (Fig. 1). (ii) Because the electronic charge density can be readily computed, is data rich, and improvement in density functional theory (DFT) predictions have been slower than for energies, we are developing techniques to predict it using graph neural networks from QMC data. We first focus on molecular systems where computational costs are lower than for solids. Application of our newly developed neural networks to ~2300 molecules of the QM9 dataset demonstrates the viability of reaching accurate predictions and accommodating the statistical nature of the training data. Models and datasets will be made openly available, and we next plan to extend the methods to more complex systems.

Relevance to MGI
Agility as well as accuracy of predicting energetics and properties plays an important role when it comes to using theory to guide new experiments or accelerate the interpretation of new synthesis or characterization methods. We combine high-throughput workflows aimed at property predictions made by highly accurate QMC methods for molecules and solids (See first CPSFM abstract) with state-of-the-art message-passing graph neural networks (GNNs) [1] to realize machine-learning surrogate models that can predict properties at the level of accuracy of high-fidelity yet costly electronic structure methods, such as QMC. This can accelerate rapid screening and discovery of new complex materials for a wide range of functional applications but requires us to identify key challenges in machine-learning noisy QMC datasets. We also make available reference QMC-quality datasets that can be used to benchmark or improve lower fidelity electronic-structure methods as well as high-throughput workflows that were used to produce those datasets, allowing reproducibility, and facilitating increased adoption of QMC.

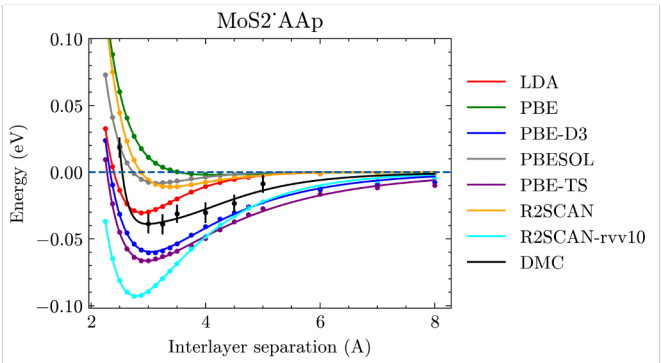


Figure 1. Binding curve of bilayer MoS_2 computed with diffusion QMC compared with different density functional approximations. We have computed binding curves and charge densities for many common 2D materials including C, BN, MoS_2, WTe_2 (unpublished).

Technical Progress
Currently, we have generated QMC energies and charge density data for over 2300 QM9 molecules and developed workflows to compute such energies for molecules as well as van der Waals bonded systems, assessing errors against a wide range of DFT functionals (Figs. 1&2). The workflows are implemented in our workflow software NEXUS [2], which can combine DFT, Quantum Chemical and QMC calculations. QMC calculations employed standard single-reference wave functions throughout; extension to multireference is left to future work.

We have implemented and trained a message-passing GNN on charge densities and quantified errors in the predicted quantities. We expect marginal improvements in predictions upon the final implementation of the GNN model. This model, where densities are sampled on a fixed grid, is uniformly applicable to molecules and solids. The same GNN representation will also be used to learn scalar quantities such as total and kinetic energies, allowing for a single representation to develop predictive machine learning (ML)-models for electronic properties of materials. The goodness-of-fit R^2 is close to 1 using these models, demonstrating its versatility in learning these different types of quantities of interest. We plan to include similar optimizations for the spin densities in addition to charge densities. This is done by considering the triplet state molecules of QM9 in addition to closed-shell singlets.

Future Plans

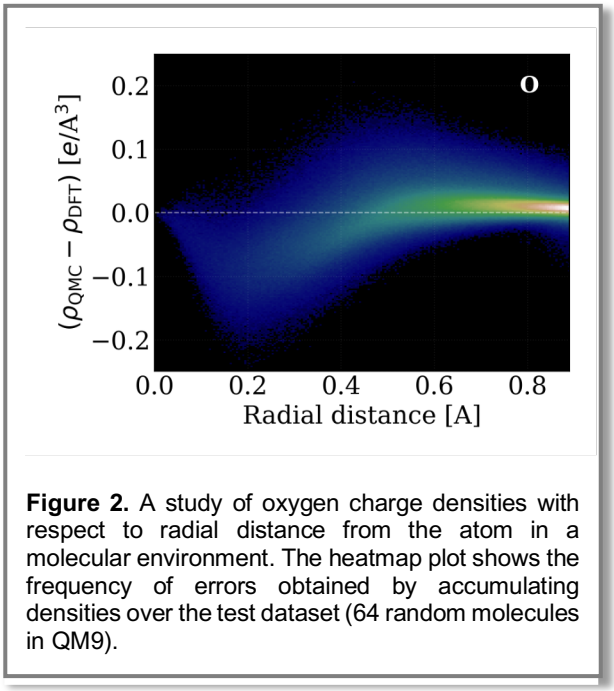


Figure 2. A study of oxygen charge densities with respect to radial distance from the atom in a molecular environment. The heatmap plot shows the frequency of errors obtained by accumulating densities over the test dataset (64 random molecules in QM9).

Our plans include extending the tools and capabilities to solid state applications. In particular, learning and predicting the QMC energies and charges densities of functional materials in periodic boundary conditions is the next step in the project. Once developed and proven, the workflows for solids will enable us to be more responsive to requests for QMC materials data for use in ML training.

Broader Impacts and Workforce Development

We are collaborating with the JARVIS team at NIST and are making QMC benchmark datasets available using their platform for a selective set of inorganic systems that are traditionally problematic for lower fidelity methods (e.g. magnetic systems, van der Waals compounds etc.). This has broader implications, for example researchers developing new functionals can now rapidly assess the DFT-errors over a standardized set of high-fidelity QMC benchmark data and compare/contrast with each existing functionals in a uniform manner. The synergistic collaborations between electronic structure experts and AI/ML experts have resulted in training new students/postdocs from disparate disciplines to combine these otherwise different skillsets.

Data Management and Open Access

Following FAIR principles, the input and output files of this project will be published in "Materials Data Facility" (MDF, https://materialsdatafacility.org/). In addition, processed charge density and energy files that are suitable for machine learning will be provided. Code snippets, scripts, and any other auxiliary tools will be included in the MDF data set and on the QMCPACK GitHub organization.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Our project establishes fundamental principles and methods for creating and sharing high-fidelity QMC datasets using automated workflows to encourage practitioners of electronic structure methods to use more readily QMC calculations. The availability of agile machine ML surrogates with the QMC-level of accuracy is expected to allow experimental researchers to more readily assess and interpret their experiments using QMC-based ML models. Further, QMC datasets and our ML-models for energies and densities are expected to be a steppingstone for developing improved electronic structure methods that can describe complex materials with a similar accuracy.

Publications and References

1. Abdulgani Annaberdiyev, Fan Shu, Victor Fung, and Panchapakesan Ganesh, *APS March Meeting 2024*, https://meetings.aps.org/Meeting/MAR24/Session/Q60.9

2. J. T. Krogel, "*Nexus: A Modular Workflow Management System for Quantum Simulation Codes*". Computer Physics Communications **2016**, 154. DOI: 10.1016/j.cpc.2015.08.012.

Three-Body Tight-Binding for Materials Design

Lead Investigator: Kevin F. Garrity, kevin.garrity@nist.gov
Participating Institutions: NIST
Source of Support: NIST
Website: https://pages.nist.gov/ThreeBodyTB.jl/
Keywords: DFT, tight-binding, high-throughput

Project Scope

The goal of this project is to develop a code that calculate materials properties for a wide range of materials three orders of magnitude faster than density functional theory (DFT), using parameterized tight-binding. We fit a model including two-body and three-body interaction for most of the periodic table, and we are testing this method for bulk materials, defects, surfaces, and at finite temperatures.

Relevance to MGI

In this work, we take advantage of the large datasets available from high-throughput computation to fit a physics-based model that describes the fundamental properties of energy, crystal structure, and electronic structure that are relevant for materials design and discovery. Because this model is much faster than traditional electronic structure and contains more physics than pure machine learning-based approaches, we can use the model to predict new materials properties in a systematic manner. As an initial project, we have applied the model to the prediction of point defect properties.

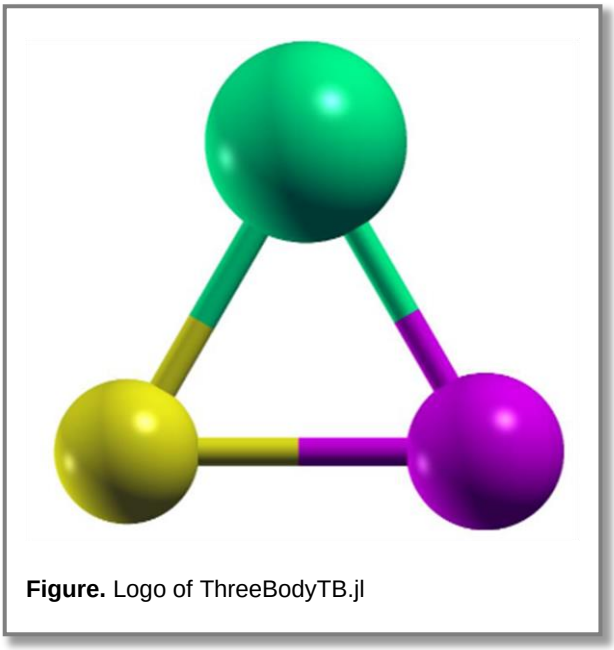


Figure. Logo of ThreeBodyTB.jl

Technical Progress

We have developed an updated parameter set including elemental, binary and ternary interactions that allows for calculating materials properties for most of the periodic table. Using this parameter set, we have performed tests of predicted energies, volumes, electronic structure, and defect energetics. In addition, we have updated our code for better performance using sparse matrix techniques and added new features including magnetism.

Future Plans

We will further test and update the current parameter set for the project. In addition, we will implement new features such as spin-orbit, linear scaling, etc.

Broader Impacts and Workforce Development

We have presented this work as part of a tutorial session at the NIST-hosted AIMS conference of Artificial Intelligence for Materials Science, and we are working to develop additional web and in-person materials to disseminate the code and ideas in this work.

Data Management and Open Access

We disseminate the code for this work via https://github.com/usnistgov/ThreeBodyTB.jl with the documentation at https://pages.nist.gov/ThreeBodyTB.jl/ . The DFT database developed for this project is available at https://jarvis.nist.gov/jarvisqetb/ . In addition, there is a python interface to the code at https://github.com/usnistgov/tb3py and a notebook teaching the code basics at https://github.com/JARVIS-Materials-Design/jarvis-tools-notebooks/blob/master/jarvis-tools-notebooks/ThreeBodyTB_julia.ipynb . Future goals include a web-interface to try the code directly.

Advancing Along the Materials Development Continuum and Partnerships to Translation

This project is being incorporated into our future semiconductor research funded by the CHIPS act. This work on multiscale modeling of semiconductor devices is in collaboration with other groups at NIST and industrial partners. This work is ongoing.

Publications and References

1. K. F. Garrity and K. Choudhary, *Fast and accurate prediction of material properties with three-body tight-binding model for the periodic table*, Phys. Rev. Mater. **7** 044603 (2023). DOI: 10.1103/PhysRevMaterials.7.044603

DMREF: Design of surface functionality through surface composition and structure

Lead Investigator: Andrew J. Gellman, gellman@cmu.edu
Participating Institutions: Carnegie Mellon University, Columbia University
Source of Support: NSF-DMREF
Website: none
Keywords: alloys, surface chemistry, catalysis, segregation, structure sensitivity

Project Scope

The project objective is to accelerate the development of complex functional surfaces such as those of alloy catalysts. We are accelerating computational prediction of surface properties while concurrently developing high throughput measurements for prediction verification. These methods are spanning parameter spaces such as alloy composition and surface structure that are intractable to traditional methods of study.

Relevance to MGI

We focus on two parameter spaces: alloy composition, $A_xB_yC_{1-x-y}$, and surface structure, M(*hkl*). Both influence surface chemistry relevant to catalysis. Both are described by continuous variables; challenging to both experiment and computation. We address both challenges. For example, comprehensive measurement of surface segregation spanning composition space in $Cu_xPd_yAu_{1-x-y}$ and $Cu_xAg_yAu_{1-x-y}$ has been completed concurrently with computational simulations of segregation. Ultimately, this cooperation will lead to accurate computational predictions of surface segregation in reactive environments where experiments have no reach. Similarly, recent developments in strategies for relaxation of molecular structures on surfaces have accelerated the ability to study surfaces with complex structure. This will aid efforts to understand a dataset measuring the kinetics of O_2 adsorption on all Cu(*hkl*) surfaces lying within 12° of the Cu(111) plane.

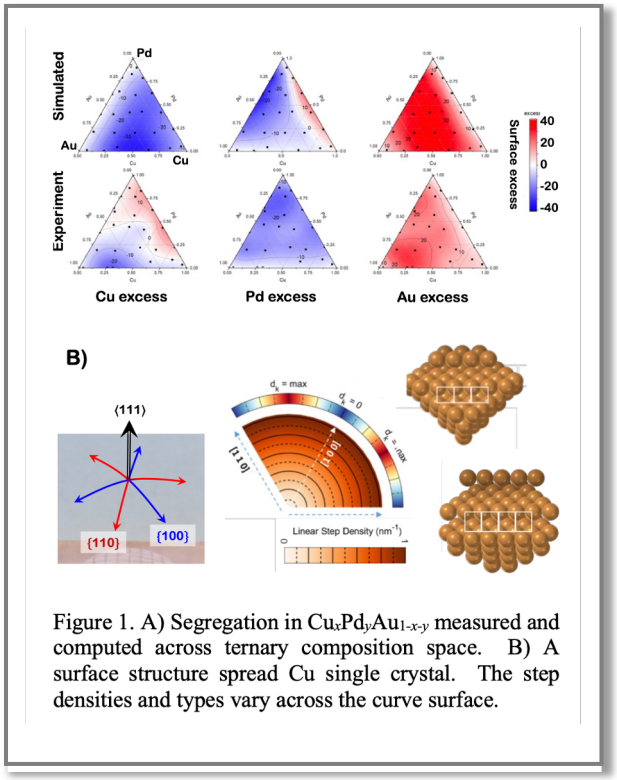


Figure 1. A) Segregation in $Cu_xPd_yAu_{1-x-y}$ measured and computed across ternary composition space. B) A surface structure spread Cu single crystal. The step densities and types vary across the curve surface.

Technical Progress

Surface Segregation. High throughput methods have been used to both measure and simulate surface segregation in $Cu_xPd_yAu_{1-x-y}$ and on $Cu_xAg_yAu_{1-x-y}$ alloys across their entire composition spaces.[1,2] These are far more comprehensive than any prior study. Initial work (Fig. 1A) revealed a discrepancy in the order of Pd and Cu segregation along the CuPd binary. Measurement shows preferential Cu segregation while the simulation shows otherwise. This has been traced to the modeling relying on simulation of an FCC(111) surface while the alloy films are polycrystalline. The predicted order of segregation of Pd versus Cu switches when the surface orientation is FCC(110).

Structure sensitivity. Using a curved Cu(*hkl*) single crystal with the (111) orientation at the center (Fig. 1B), we have mapped the kinetics of O_2 adsorption across surface orientation space with unparalleled fidelity and resolution. These reveal clearly that the rate of dissociative adsorption of O_2 is lowest on the Cu(111) surface. It increases monotonically as the step density increases towards the edges of the curved surface, however, it is also clear that (100) steps are much more active than (110) steps. We are now starting to explore the origins of these structure

sensitive differences in reactivity using simulations. These simulations on complex high Miller index surfaces will benefit from some of the methods that we have developed for acceleration of geometry optimization.[3]

Degree of rate control. We have demonstrated the use of automated differentiation as an effective method for accurate calculation of derivatives such as those used in the definition of the degree of rate control.[4] This has been used to analyze a 17-step mechanism for propylene epoxidation, one of the catalytic processes being probed experimentally.[5,6] Our analysis has elucidated the three steps with dominant degrees of rate control. These three steps are the primary dictators of the overall reaction rate. The value of this approach lies in pointing modeling efforts towards those steps in a process whose acceleration will yield the greatest impact on overall reaction rate.

Future Plans

Our plans for the future include the application of accelerated simulation methods to the surface structure sensitivity of O_2 adsorption on Cu(*hkl*) surfaces. In addition, we will generate measurements of catalytic surface reaction kinetics spanning alloy composition space for reactions such as propylene and propyne hydrogenation.

Broader Impacts and Workforce Development

To date the program has graduated 4 students: Dr. Zhitao Guo (PhD, CMU), Dr. Yilin Yang (PhD, CMU), Mr. Matt Adams (MS, CMU) and Mr. Marcus Yu (BS, CMU joining Columbia ChE PhD program). Four more PhD students are currently being trained via this project. The subprojects studying 'alloy segregation' and developing the use of automated differentiation for determination of 'degrees of rate control' have been disseminated to the general public via YouTube videos (segregation - https://youtu.be/lbNANFj928k, degree of rate control - https://youtu.be/2PIEJp8CGNM). Three students have been allotted instrument time at the Center for Functional Nanomaterials at Brookhaven National Lab.

We developed a cloud-based computational environment using Jupyter HUB that allowed us to support several workforce development events. First, we ran a software workshop at the 2023 Fall ACS meeting on using the Open Catalyst Project for molecular simulation (https://github.com/Open-Catalyst-Project/tutorial). The computational environment allowed local and remote attendees to run simulations using GPUs on a range of problems including computing adsorption energies and screening catalysts. Second, we ran an introduction to Python and data science for a high school summer program. About 80 students were able to log in to the Jupyter HUB to practice solving engineering and science programs. Finally, we translated the success from these examples to supporting a computational course for a complete semester using Jupyter HUB.

Data Management and Open Access

Data and software are being made openly available at: https://github.com/ulissigroup, https://ulissigroup.cheme.cmu.edu/software-data/, https://github.com/yilinyang1/NN-ensemble-relaxer.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Impact on materials R&D will arise from transfer and application of the methods (both experimental and computational) developed in the course of this project. The work so far has led to collaborations with researchers at Brookhaven NL and elsewhere.

Publications and References

1. C. Yin, Z. Guo, A.J. Gellman, "*Surface Segregation Across Ternary Alloy Composition Space: $Cu_xAu_yPd_{1-x-y}$*" Journal of Physical Chemistry – C **124**, 10605 – 10614 (2020) (10.1021/acs.jpcc.0c02058?ref=pdf)
2. Yilin Yang, Zhitao Guo, Andrew Gellman and John Kitchin, *Simulating segregation in a ternary Cu-Pd-Au alloy with density functional theory, machine learning and Monte Carlo simulations*, J. Phys. Chem. C, (2022). https://pubs.acs.org/doi/abs/10.1021/acs.jpcc.1c09647
3. Yang, Y., Omar A. Jiménez-Negrón, and Kitchin, J. R., *Machine-learning accelerated geometry optimization in molecular simulation*, Journal of Chemical Physics, **154**(23), 234704 (2021). http://dx.doi.org/10.1063/5.0049665

4. Yilin Yang, Siddarth K. Achar, John R. Kitchin, *Evaluation of the Degree of Rate Control via Automatic Differentiation*, AIChE Journal, (2022). https://doi.org/10.22541/au.162855056.60483260/v1.
5. W.N. Porter, Z. Lin and J.G. Chen, "*Experimental and theoretical studies of reaction pathways of direct propylene epoxidation on model catalyst surfaces*", Surface Science Reports **76** (2021) 100524
6. W.N. Porter, Z. Lin and J.G. Chen, "*Elucidating interactions of the epoxide ring on Pt(111) by comparing reaction pathways of propylene oxide and 1-epoxy-3-butene*". Journal of Vacuum Science and Technology A (Special issue honoring Pat Thiel) **39** (2021) 063214.
7. Yilin Yang, Mingjie Liu, John Kitchin, *Neural Network Embeddings based Similarity Search Method for Catalyst Systems*, Digital Discovery, **1** (2022), 636-644. https://doi.org/10.1039/D2DD00055E.
8. N. Shukla, M. Yu, A. Pradhan, Y. Han, A.J. Gellman, *Chirality Retention in Aqueous Propylene Oxide Hydration: Chirality of the Transition State* Israel Journal of Chemistry **61**, (2021), 743–749 (https://doi.org/10.1002/ijch.202100098)
9. Y. Yang, Z. Guo, A.J. Gellman, J.R. Kitchin, "*Simulating Segregation in a Ternary Cu–Pd–Au Alloy with Density Functional Theory, Machine Learning, and Monte Carlo Simulations*", Journal of Physical Chemistry C 126(4), (2022), 1800-1808, (https://doi.org10.1021/acs.jpcc.1c09647)
10. William Porter, Hilda Mera, Wenjie Liao, Zhexi Lin, Ping Liu, John Kitchin and Jingguang Chen, *Controlling Bond Scission Pathways of Isopropanol on Fe- and Pt-Modified Mo2N Model Surfaces and Powder Catalysts*, **14** (2024), 1653-1662. https://pubs.acs.org/doi/10.1021/acscatal.3c04700.
11. K. Broderick, R. Burnley, A.J. Gellman, J.R. Kitchin "*Surface Segregation Studies in Ternary Noble Metal Alloys: Comparing DFT and Machine Learning with Experimental Data*" ChemPhysChem, (2024), e202400073, (https://doi.org/10.1002/cphc.202400073)
12. K. Abdelmaqsoud, M. Radetic, C. Fernández-Cabán, M. Widom, J.R. Kitchin, A.J. Gellman "*Structure Sensitive Reaction Kinetics of Chiral Molecules on Intrinsically Chiral Surfaces*" Journal of the American Chemical Society, in review

Electron transport from first principles with EPW

Lead Investigator: Feliciano Giustino, fgiustino@oden.utexas.edu
Participating Institutions: The University of Texas at Austin (Feliciano Giustino), University of Michigan at Ann Arbor (Emmanouil Kioupakis), Binghamton University (Roxana Margine)
Source of Support: DOE-BES
Website: https://epw-code.org/
Keywords: Electron-phonon interactions, electron transport, electronic properties, open-source code development

Project Scope

The broad goal of the EPW project (DOE/BES CMS Award DE-SC0020129) is to develop and apply first-principles tools to calculate electronic and optoelectronic properties related to electron-phonon interactions. This poster focuses on efforts within this project to characterize the electronic transport properties of metals and semiconductors. We solve the Boltzmann transport equation (BTE), which describes the response of the electron distribution to scattering processes and external fields, to calculate conductivity and mobility values. The parameters of the BTE are from first-principles calculations, enabling predictive accuracy that we validate through comparison against experimental data.

Relevance to MGI

This project is part of the Computational Materials Sciences (CMS) program, which was started in 2015 as part of the MGI. In alignment with the goals of the CMS program, we develop open-source software that leverages high-performance computing power to predictively model the properties of matter at the atomic scale. We are continuously expanding the capabilities of the code to capture more properties and at higher levels of accuracy. For example, a new module has been added to calculate polaronic states in insulators and the transport module has been augmented to include the effects of ionized-impurity scattering. In addition to expanding the capabilities of the code, we are refactoring the code to take advantage of the emerging exascale computing power by adding multi-level OpenMP/MPI parallelization. Code development is complemented by engagement with the user community through extensive documentation, online tutorials, YouTube lectures, a lively user forum, and the organization of multiple summer schools both virtual and in person. Through improvement of the code and increased involvement of the community, we will accelerate the characterization and design of new electronic materials.

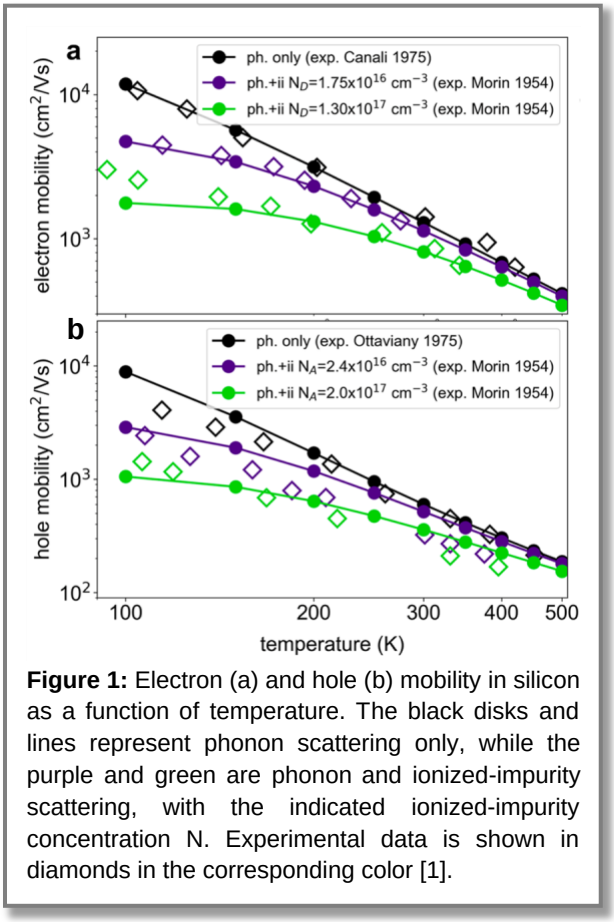


Figure 1: Electron (a) and hole (b) mobility in silicon as a function of temperature. The black disks and lines represent phonon scattering only, while the purple and green are phonon and ionized-impurity scattering, with the indicated ionized-impurity concentration N. Experimental data is shown in diamonds in the corresponding color [1].

Technical Progress

We have extended the existing electron transport module, which previously only calculated phonon-limited transport, to also include the effects of ionized-impurity scattering in semiconductors [2]. While the phonon-limited mobility represents the intrinsic upper limit of transport in a semiconductor, many semiconductors are doped and the ionized dopants will serve as an additional source of scattering that will impact the mobility. We include ionized-impurity scattering by calculating the partial ionized-impurity scattering rate from a randomized distribution of point charges and incorporating this scattering rate in the solution of the BTE. Through selection of which partial scattering rates to include in the BTE, we can calculate phonon-limited, ionized-impurity-limited, and total mobility values. We applied this to silicon, silicon carbide,

gallium phosphide, and tin dioxide [2, 3]. With the inclusion of ionized-impurity scattering, we can compare our calculated mobility values to experimental measurements of doped samples, as seen in Figure 1.

Future Plans

Future plans for the transport module focus primarily on the development of a solution to the nonlinear BTE to model transport in the regime of high electric fields. Currently implemented is the linearized BTE which describes the first-order response to an external electric field, which is valid in the low-field regime. However, in the high-field regime the response of the electron distribution is no longer linear with respect to the electric field and the full nonlinear BTE must be used to correctly describe the system. We are currently exploring multiple avenues to solve the nonlinear BTE in order to study carrier transport under high electric fields. This development will allow us to compute velocity-field curves in a range of semiconductors. These approaches will be validated against experimental data for well-studied semiconductors and then used to explore promising wide band gap and ultra-wide band gap semiconductors that are well-suited to high-power applications.

Additionally, at a broader scope, there is the planned improvement of parallel performance of all the EPW modules via multi-level OpenMP/MPI parallelization.

Broader Impacts and Workforce Development

During June 2023 we organized a 5-days (06/05 to 06/09/2023) virtual summer school that, for the first time, combined many-body physics with the BerkeleyGW code and electron-phonon physics with the EPW code. This school consisted of 5 days of morning lectures and afternoon hands-on tutorials, and hosted 152 participants from across the globe. All materials from this school have been made available through the EPW website: https://epw2023.oden.utexas.edu. During June 2024 we organized an in-person 7-days summer school (06/10 to 06/16/2024) on electron-phonon interactions and many-body perturbation theory from first principles. The school consisted of morning lectures, afternoon hands-on tutorials covering codes including Quantum ESPRESSO, wannier90, EPW, and BerkeleyGW and the related theories. We welcomed 127 participants to UT Austin (103 in person attendees and 24 instructors.) and 577 virtual attendees on Zoom platform. All lectures, tutorials, videos have been made available through the school website: https://epw2024.oden.utexas.edu/index.php.

Data Management and Open Access

All software developments of this project are made fully available to the community via two channels: 1) periodic releases of new software versions. We currently have two annual releases, in the Spring and in the Fall. The latest version EPW 5.8 was released during December 2023 (https://docs.epw-code.org/doc/Releases.html), and EPW 5.9 is planned to be released in July 2024. Anyone can freely download and use the code without any registration or email requests. Users are encouraged to interact with developers via the user forum (https://forum.epw-code.org) which currently counts 3800+ posts and 650+ members. 2) The gitlab repository of the official version of the code is accessible to all without limitation: https://gitlab.com/QEF/q-e/-/tree/develop/EPW. This version is updated in real time and can be used by more advanced users who are interested in the code structure. The code is released under GNU GPL license.

Advancing Along the Materials Development Continuum and Partnerships to Translation

This project enables predictive calculations of transport properties of promising materials for electronic devices, facilitating faster materials discovery and device design processes. Our software is available open-source and supported with thorough documentation, tutorials and examples, and a summer school to encourage the broader research community to make use of the tools we are developing. We expect that these new capabilities developed in this project will facilitate new partnerships for discovery of materials with superior transport properties and we are currently in the process of exploring these opportunities.

Publications and References

1. H. Lee, S. Poncé, K. Bushick, S. Hajinazar, J. Lafuente-Bartolome, J. Leveillee, C. Lian, J.-M. Lihm, F. Macheda, H. Mori, H. Paudyal, W.H. Sio, S. Tiwari, M. Zacharias, X. Zhang, N. Bonini, E. Kioupakis, E.R. Margine, and F. Giustino, *Electron–phonon physics from first principles using the EPW code*, Npj Comput Mater **9** (1), 1–26 (2023). DOI: 10.1038/s41524-023-01107-3

2. J. Leveillee, X. Zhang, E. Kioupakis, and F. Giustino, *Ab initio calculation of carrier mobility in semiconductors including ionized-impurity scattering*, Phys. Rev. B **107** (12), 125207 (2023). DOI: 10.1103/PhysRevB.107.125207

3. A. Wang, K. Bushick, N. Pant, W. Lee, X. Zhang, J. Leveillee, F. Giustino, S. Poncé, E. Kioupakis, *Electron mobility of SnO_2 from first principles*, Appl. Phys. Lett. **124** (17), 172103 (2024). DOI: 10.1063/5.0198885

Ab initio phonon-mediated optical processes with EPW

Lead Investigator: Feliciano Giustino, fgiustino@oden.utexas.edu
Participating Institutions: The University of Texas at Austin (Feliciano Giustino), The University of Michigan at Ann Arbor (Emmanouil Kioupakis), Binghamton University-SUNY (Elena Roxana Margine)
Source of Support: DOE-BES
Website: https://epw-code.org/
Keywords: Electron-phonon interactions, phonon-assisted optical processes, optoelectronic materials, open-source code development

Project Scope

In this project, which is part of the collaborative project funded by DOE/BES CMS under Award DE-SC0020129, we focus on understanding phonon-mediated optical processes using first-principles techniques to improve rational design of optoelectronic devices. Traditional density-functional theory (DFT) and many-body perturbation-theory (MBPT) approaches typically decouple electron and ion motions, treating ions as classical particles, and thus missing indirect optical processes mediated by electron-phonon interactions. We develop novel theories and computational approaches based on time-dependent perturbation theory, special displacements in supercells, and quasi-degenerate perturbation theory to investigate complex optical processes, including free-carrier absorption, optical processes in quasi-direct materials, and effects of temperatures. These approaches are implemented in our open-source code EPW[4] (https://epw-code.org/), which is a collaborative effort between multiple teams across the world aiming to understand electron-phonon interactions from first principles.

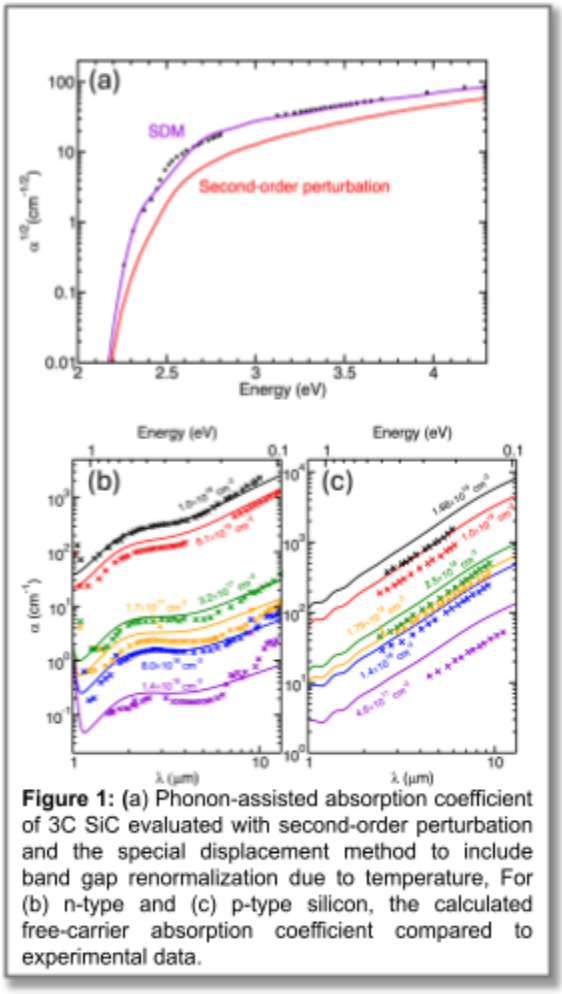


Figure 1: (a) Phonon-assisted absorption coefficient of 3C SiC evaluated with second-order perturbation and the special displacement method to include band gap renormalization due to temperature, For (b) n-type and (c) p-type silicon, the calculated free-carrier absorption coefficient compared to experimental data.

Relevance to MGI

This project belongs to DOE's Computational Materials Sciences (CMS) program which started in 2015 as part of the MGI. The overarching goal of the CMS program is to develop validated community codes and databases to underpin the predictive design of functional materials. Our team contributes to the DOE CMS and the MGI along two complementary directions: 1) Continuous expansion of the predictive capabilities of the EPW software, for example by adding new modules to perform predictive *ab initio* calculations of optical spectra at finite temperature as well as conductive materials such as doped semiconductors and metals. 2) To refactor EPW in preparation of the exascale transition. These efforts are complemented by a strong engagement with the user community, via extensive documentation, online tutorials, YouTube lectures, a lively user forum, and the organization of multiple summer schools both virtual and in person. These advances in methodology, software, and training will accelerate the development of new materials in optoelectronics, energy harvesting, and energy-efficient lighting.

Technical Progress

We have developed the indirect optics modules in the EPW code to study phonon-assisted absorption and free-carrier absorption based on second-order perturbation theory. We studied indirect optical properties in 4H Si[1] and SiC polytypes[3] [See Fig.1(a)], and we show that our tool enables predictions of the optical response of new polytypes of known semiconductors for understanding their potential applications. Within the same

framework, we studied free-carrier absorption doped silicon and noble metals, and we demonstrated excellent agreement compared to experimental measurements[2] [See Fig.1(b),(c)], and the necessity of the inclusion of both single-particle contribution and resistive contribution in evaluating free-carrier absorption. The development quantifies the optical loss as well as provides a contact-free way of characterizing carrier concentrations. We developed several approaches to characterize indirect absorption in quasi-direct materials and to include finite-temperature effects, including optical absorption via quasi-degenerate perturbation theory[5], and the special displacement method.[7]

Future Plans

In the future, we will prioritize the following tasks: (1) Co-development between the teams to enable free-carrier absorption via advanced theory such as the special displacement approach and the quasi-degenerate perturbation theory. (2) Calculations of carrier-density dependent absorption for a wide range of oxide and III-V semiconductor materials. (3) Development and validation of the functionality to study phonon-mediated two-photon absorption. (4) Finalize and publish the result of optical responses of metallic materials. and (5) Improvement of parallel performance of the modules via multi-level parallelization.

Broader Impacts and Workforce Development

During June 2023 we organized a 5-days (06/05 to 06/09/2023) virtual summer school that, for the first time, combined many-body physics with the BerkeleyGW code and electron-phonon physics with the EPW code. This school consisted of 5 days of morning lectures and afternoon hands-on tutorials, and hosted 152 participants from across the globe. All materials from this school have been made available through the EPW website: https://epw2023.oden.utexas.edu. During June 2024 we organized an in-person 7-days summer school (06/10 to 06/16/2024) on electron-phonon interactions and many-body perturbation theory from first principles. The school consisted of morning lectures, afternoon hands-on tutorials covering codes including Quantum ESPRESSO, wannier90, EPW, and BerkeleyGW and the related theories. We welcomed 127 participants to UT Austin (103 in person attendees and 24 instructors.) and 577 virtual attendees on Zoom platform. All lectures, tutorials, videos have been made available through the school website: https://epw2024.oden.utexas.edu/index.php.

Data Management and Open Access

All software developments of this project are made fully available to the community via two channels: 1) periodic releases of new software versions. We currently have two annual releases, in the Spring and in the Fall. The latest version EPW 5.8 was released during December 2023 (https://docs.epw-code.org/doc/Releases.html), and EPW 5.9 is planned to be released in July 2024. Anyone can freely download and use the code without any registration or email requests. Users are encouraged to interact with developers via the user forum (https://forum.epw-code.org) which currently counts 3800+ posts and 650+ members. 2) The gitlab repository of the official version of the code is accessible to all without limitation: https://gitlab.com/QEF/q-e/-/tree/develop/EPW. This version is updated in real time and can be used by more advanced users who are interested in the code structure. The code is released under GNU GPL license.

Advancing Along the Materials Development Continuum and Partnerships to Translation

This project enables advanced calculations of temperature- and doping-dependent optical properties for direct, indirect, and quasi-direct materials. We expect that these new capabilities developed in this project will facilitate new partnerships for rational design of optoelectronics with a broad range of candidate materials, and we are currently in the process of exploring these opportunities.

Publications and References

[Most relative publications in the past two years are included in order of relevance to this poster.]

1. X. Zhang, E. Kioupakis. Electronic, direct optical, and phonon-assisted optical properties of 4H Si from first principles. *AIP Adv.* 14, 3: 035149 (2024). DOI: https://doi.org/10.1063/5.0179454

2. X. Zhang, G. Shi, J. A. Leveillee, F. Giustino and E. Kioupakis,“Ab initio theory of free-carrier absorption in semiconductors”, Phys. Rev. B 106.20, 205203, (2022), DOI: https://doi.org/10.1103/PhysRevB.106.205203

3. X. Zhang and E. Kioupakis, Phonon-assisted optical absorption of SiC polytypes from first principles, Phys. Rev. B 107, 115207 (2023), DOI: https://doi.org/10.1103/PhysRevB.107.115207
4. H. Lee, S. Poncé, *et al.* Electron–phonon physics from first principles using the EPW code. *npj Comput Mater* 9, 156 (2023). DOI: https://doi.org/10.1038/s41524-023-01107-3
5. S. Tiwari, E. Kioupakis, J. Menendez, and F. Giustino, Unified theory of optical absorption and luminescence including both direct and phonon-assisted processes, Phys. Rev. B 109, 195127 (2024),
DOI: https://doi.org/10.1103/PhysRevB.109.195127
6. J. Leveillee, X. Zhang, E. Kioupakis, and F. Giustino, Ab initio calculation of carrier mobility in semiconductors including ionized-impurity scattering, Phys. Rev. B 107, 125207, (2023), DOI: https://doi.org/10.1103/PhysRevB.107.125207
7. M. Zacharias and F. Giustino, Theory of the special displacement method for electronic structure calculations at finite temperature, Phys. Rev. Research 2, 013357 (2020), DOI: https://doi.org/10.1103/PhysRevResearch.2.013357

Machine Learning and Robotics for the Data-Driven Design of Protein-Polymer Hybrid Materials

Lead Investigator: Adam Gormley, adam.gormley@rutgers.edu
Participating Institutions: Rutgers University and Princeton University
Source of Support: NSF-DMREF 2118860-1
Website: https://dmref.org/projects/155
Keywords: Polymers, proteins, excipients, formulation, automation, machine learning.

Project Scope

Proteins perform versatile functions with high efficiency and exquisite selectivity. Our ability to engineer proteins has resulted in a transformative array of products from life supporting medicines to fine chemicals from green industrial processes. However, the marginal stability of proteins is a major challenge toward their incorporation in robust materials that can withstand harsh, non-biological conditions, e.g., high temperature and/or organic co-solvents. Therefore, there is a very large unmet need for producing tailor-made protein-polymer hybrids (PPH) whose interactions are highly specific, predictable, and optimizable. To address this unmet need, this project combines automation, machine learning, and molecular dynamics simulations to design novel PPH materials.

Figure. The goal of this NSF DMREF project is to use automation driven by machine learning to design polymer-protein hybrid materials.

Relevance to MGI

This project closely integrates high throughput data generation via automation, machine learning, molecular dynamics simulations, and protein engineering. Each aspect of this project feeds the other with data to create a closed-loop discovery workflow with data curation and labeling at the center. This creates a project ecosystem with well labeled material data. As new data is collected, the team takes an informatics approach to analyze the results and publish them open access. This approach aligns with the MGI mission.

Technical Progress

We have established routine protocols and workflows that enable rapid experimental synthesis and assessment. Given experimental bandwidth for polymer synthesis in 96-well plates, we have tested four distinct enzymes: chondroitinase ABC (ChABC), horseradish peroxidase (HRP), glucose oxidase (GOx), and lipase (Lip). For each enzyme, approximately 600 unique copolymers were tested, with experimental data often collected in triplicate. These efforts are likely the most extensive ex nihilo dataset involving experimental copolymer synthesis and characterization to-date.

We have successfully demonstrated our proof-of-principle and key hypothesis that our closed-loop discovery process, guided by machine learning, will yield tailored PPHs. For each of the four enzymes, our design goal was maximizing retained enzyme activity (REA) following thermal stressing; for reference, proteins without any polymers exhibit REA = 0% post thermal stress and REA < 100% indicates fractional activity compared to native enzyme function. Ultimately, our data-driven discovery process led to identification of tailored copolymers that led to significant REA for each enzyme. The performance of these designed PPHs was particularly notable compared

to more traditional brute-force, systematic chemical screens. The top performing PPHs exhibited remarkable REA values of 141% (ChABC), 93.1% (HRP), 67.4% (GOx), and 107.9% (Lip). Cross-evaluation studies confirmed that designed copolymers uniquely stabilized the target enzyme—proving our central hypothesis.

Future Plans

Subcutaneous delivery of monoclonal antibodies in pre-filled autoinjectors are enabling at-home self-administration of crucial anti-inflammatory and oncological therapies. However, as the demand for subcutaneous dosing increases, so does the need for stable bioformulations which can enable ultrahigh concentrations, low viscosity, and drug stability; requirements for pre-filled autoinjectors. While rational design and design of experiment (DOE) approaches are utilized to screen for effective formulas, data science techniques such as artificial intelligence / machine learning (AI/ML) may be ideally suited to drive these formulation campaigns. To assess the capacity for ML guided mAb formulation, we aim to expand on our previous "Design-Build-Test-Learn" (DBTL) strategies for protein stabilization (Advanced Materials 2022 and Advanced Healthcare Materials 2022) to develop methods for on-demand mAb formulation. This work aims to both: i) employ ML to enable rapid high-performance formulations with generally recognized as safe (GRAS) excipients, and ii) design novel polymer excipients by ML to modulate poor formulation behaviors.

Broader Impacts and Workforce Development

DMREF program continues to host two students, Ms. Grace Palahnuk and Ms. Sachely Antuna from The College of New Jersey (TCNJ), our collaborating undergraduate institution. Grace worked in Gormley Lab on studying polymer-enzyme complex activity and polymer combinatorial synthesis. Over the next year, she will evaluate the effect of monomer composition and degree of polymerization on retained enzymatic activity of polymer-enzyme complexes during exposure to denaturing temperatures. Sachely worked in Murthy lab on the biophysical characterization of protein-enzyme complexes. She accompanied the team on two visits to NSLSII, collected SAXS data on PPHs and analyzed data on lipase-polymer complexes. She also carried out quartz crystal microbalance with dissipation (QCMD) on these complexes. This research of both the students was presented at the BMES 2023 Annual Meeting as a poster presentation.

Data Management and Open Access

The DMREF team is fully committed to making key research outputs publicly accessible and useful to the community. Therefore, datasets generated from supported research have been published to DataSpace with registered DOIs for long-term preservation and access (10.34770/h938-nn26, 10.34770/chzn-mj42,10.34770/a2db-gy35). The data is also hosted with accompanying code demonstrating the training and implementation of machine learning models on GitHub (github.com/webbtheosim/PPH_public, github.com/webbtheosim/featurization).

Advancing Along the Materials Development Continuum and Partnerships to Translation

This project has resulted in a startup company named Plexymer, Inc. The lead PI Gormley is a cofounder of this company. It aims to apply the methods developed in this project to formulate proteins for advanced applications. Plexymer has licensed the main intellectual property from Rutgers and is working with large companies for materials synthesis and protein formulation.

Publications and References[1-7]

1. **Gormley, A. J.**; Webb, M. A., Machine learning in combinatorial polymer chemistry. *Nature Reviews Materials* **2021,** *6*, 642-644. PMC8356908.
2. Kosuri, S.; Borca, C. H.; Mugnier, H.; Tamasi, M.; Patel, R. L.; Perez, I.; Kumar, S.; Finkel, Z.; Schloss, R.; Cai, L.; Yarmush, M. L.; Webb, M. A.; **Gormley, A. J.**, Machine-assisted discovery of chondroitinase ABC complexes towards sustained neural regeneration. *Advanced Healthcare Materials* **2022,** *11*, 2102101. PMC9119153.
3. Meyer, T. A.; Ramirez, C.; Tamasi, M. J.; **Gormley, A. J.**, A user's guide to machine learning for polymeric biomaterials. *ACS Polymers Au* **2022,** *3* (2), 141-157.
4. Tamasi, M.; Patel, R.; Borca, C.; Kosuri, S.; Mugnier, H.; Upadhya, R.; Murthy, N. S.; Webb, M.; **Gormley, A. J.**, Machine learning on a robotic platform for the design of polymer-protein hybrids. *Advanced Materials* **2022,** *34*, 2201809. PMC9339531.

5. Tamasi, M. J.; **Gormley, A. J.**, Biologic formulation in a self-driving biomaterials lab. *Cell Reports Physical Science* **2022,** *3* (9), 101041. PMC Journal - In Process.
6. Lee, J.; Mulay, P.; Tamasi, M. J.; Yeow, J.; Stevens, M. M.; **Gormley, A. J.**, A fully automated platform for photoinitiated RAFT polymerization. *Digital Discovery* **2023,** *2*, 219-233. PMC Journal - In Process.
7. Upadhya, R.; Di Mare, E.; Tamasi, M. J.; Kosuri, S.; Murthy, N. S.; **Gormley, A. J.**, Examining polymer-protein biophysical interactions with small-angle x-ray scattering and quartz crystal microbalance with dissipation. *Journal of Biomedical Materials Research Part A* **2023,** *111* (4), 440-450. PMC Journal - In Process.

Hybrid Materials for Superfluorescent Quantum Emitters

Lead Investigator: Kenan Gundogdu, kgundog@ncsu.edu
Participating Institutions: North Carolina State University, Duke University, University of North Carolina at Chapel Hill
Source of Support: NSF-DMREF
Website: https://hybrid3.duke.edu/
Keywords: Superfluorescence, hybrid metal halide perovskites

Project Scope

This project aims to accelerate the discovery of a new class of quantum materials exhibiting superfluorescence (SF) at room temperature and above. The research will focus on two main objectives: identifying material requirements for observing a macroscopically coherent superradiant state and producing experimental and computational data linking material properties such as chemical composition, morphological structure, and crystal dimensionality to their emission spectra and SF's temporal and spatial coherence properties. The target materials will be hybrid metal halide perovskites (HMHP). A key outcome is to create a comprehensive, accessible, and reusable database to aid in designing quantum materials exhibiting high-temperature SF.

Relevance to MGI

The research program relies on synergistic collaboration of four groups in material synthesis (So, NCSU), theory and computation (Blum, Duke, and Kanai, UNC-CH), and quantum properties characterization (Gundogdu, NCSU). To excel in the project, the team will interact following the organizational structure including four work packages: Work package 1 (WP.1) involves the material synthesis activities led by So and characterizing HMHP of different dimensionalities and establishing a correlation with their SF characteristics. We will quantify the SF characteristics with experiments in WP.2 led by Gundogdu. They specifically use ultrafast optical measurements to investigate optical/electronic processes in HMHP and establish the structure property relationship in materials that exhibit superradiant phase transition. WP.3, led by Blum and Kanai, involves the first-principles calculations and associated semiempirical modeling (towards larger scales), revealing the dependence of SF characteristics' on fundamental electronic and lattice properties. WP.4 lays out the systematic data collection and dissemination strategy led by Blum with his HybriD3 database development. An important aspect of the project will be delivery of significant data about formation of quantum collective states. Computing many body states and predicting the material properties that enable collective quantum phenomena is a major challenge in condensed matter. The work packages are organized to contribute overcoming this challenge.

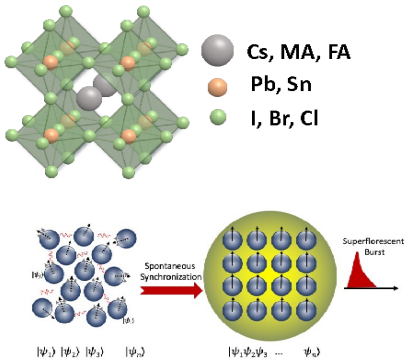


Fig 1: HMMP material platform for discovering new superfluorescent materials. Schematic illustration of superfluorescence.

Technical Progress

To achieve our first milestone, we have studied the synthesis of high-performing perovskite quantum emitters with different inorganic cages BX6 with quasi-2D PEA:$CsPbBr_3$ as our starting material[1]. In this study, the three quasi-2D perovskite samples with different halide compositions are PEA:$CsPbBr_2Cl_1$, PEA:$CsPbBr_3$, and PEA:$CSPbBr_2I_1$. The substitutional halide group significantly influences the intralayer interaction of the bulky cations via hydrogen bonding. By incorporating bulky cation halides (RX or RX2) into the precursors, quasi-2D perovskite films can be prepared by one-step spin-coating. We were able to produce samples that exhibit SF. Initially we focused on 78K measurements because not all of these materials exhibit SF at room temperatures. We found significant differences in the time revolution of SF dynamics. For instance, the PEA:$CsPbBr_2Cl_1$ thin film

has the shortest delay time of 10 ps at the threshold. Whereas the iodine mixed sample has the longest delay at the threshold density. The detailed analysis of the SF dynamics in these materials give essential information for understanding the correlation between material characteristics and collective coherence. Furthermore, we have also studied the influence of composition and deposition parameters on the photostability of the PEA:$CsPbBr_3$ samples. The preliminary results show that the composition of precursors affects the characteristics of perovskite samples. The parameters related to the deposition, such as the annealing time and temperature, the encapsulation, the substrate, and the ambient environment during the spin-coating, are important factors in the photostability of the samples. For future plans, we will study the finding of the optimum conditions for the most photostable of other mixed halide samples. Then, we will focus on changing the composition of HMHP with the A-site cation and the bulky cation (R-site).

Future Plans

We will continue the study of quasi-2D PEA:$CsPbBr_3$ and its variations which are , A-site cation, and the bulky cation (R-site). The critical hypothesis behind this selection is that the structure, dynamical properties, and detailed morphology of HMHP are related to the observed high temperature SF. Therefore, manipulating components that influence structural confinement, rigidity, or phonon characteristics will allow one to extend and refine the underlying macroscopic quantum regime rationally. The study will focus on a systematic and iterative approach to designing superfluorescent materials with optimized SF emission characteristics. Starting with materials exhibiting room-temperature SF, we will gradually modify the materials using solution-processing and post-processing procedures.

Broader Impacts and Workforce Development

Our education goal is to foster a research environment where participants from diverse backgrounds collaborate on complex scientific and technological problems. We have designed an education and training program reflecting the team's diverse experience and cross-disciplinary interaction. Since 2017, we have organized training workshops as part of our previous DMREF program. These workshops reflect project-based learning achieved during research activities, helping participants develop intuition about scientific problems and integrate theory and experiment in data-driven research. The workshops include discussion sessions, short courses, and hands-on activities targeting early-career researchers such as graduate students, postdocs, and advanced undergraduates. We will continue these workshops. Our efforts will promote broad participation across gender, racial, ethnic, geographic, and economic lines. For data technologies and training, the data produced in this program will be made accessible through the HybriD3 database.

Data Management and Open Access

The team instigated the open database "HybriD3"[2] which is a curated database of hybrid organic-inorganic semiconductors and their properties, with the flexibility to incorporate essentially any reproducible property of a material, including associated contexts such as synthesis and experimental and computational approaches. The team continues to develop the underlying open-source software stack called MatD3. As a resource, the HybriD3 database is intended to be an addition to, not a replacement of, other materials databases. For example, the HybridD3 data will also be incorporated into the industry-leading **Springer Materials** database, providing sustainability beyond the lifespan of a single PI or server hosted at a university.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Superfluorescence is a quantum optical phenomenon that gained significant interest in the community with the recent demonstrations in the perovskite materials[1,3-5]. Its potential for emerging quantum applications depends on usability of the quantum coherent state and the resulting radiated photons as well as synthesizing new robust materials that exhibit this phenomenon at high temperatures. While the DMREF program focuses on this last aspect, the teams actively working on characterizing properties of superfluorescence and resulting material behavior emerging quantum applications. We will pursue new funding opportunities accordingly.

Publications and References

1. M. Biliroglu, G. Findik, J. Mendes, D. Seyitliyev, L. Lei, Q. Dong, Y. Mehta, V. V. Temnov, F. So, K. Gundogdu, Room-temperature superfluorescence in hybrid perovskites and its origins. *Nature Photonics* **16**, 324-329 (2022).
2. R. Chakraborty, V. Blum. Curated materials data of hybrid perovskites: approaches and potential usage. *Trends in Chemistry.* **5(10)**, 720-733 (2023). https://doi.org/10.1016/j.trechm.2023.08.005
3. I. Cherniukh, G. Rainò, T. Stöferle, M. Burian, A. Travesset, D. Naumenko, H. Amenitsch, R. Erni, R. F. Mahrt, M. I. Bodnarchuk, Perovskite-type superlattices from lead halide perovskite nanocubes. *Nature* **593**, 535-542 (2021).
4. G. Rainò, M. A. Becker, M. I. Bodnarchuk, R. F. Mahrt, M. V. Kovalenko, T. Stöferle, Superfluorescence from lead halide perovskite quantum dot superlattices. *Nature* **563**, 671-675 (2018).
5. G. Findik, M. Biliroglu, D. Seyitliyev, J. Mendes, A. Barrette, H. Ardekani, L. Lei, Q. Dong, F. So, K. Gundogdu, High-temperature superfluorescence in methyl ammonium lead iodide. *Nature Photonics* **15**, 676-680 (2021).

Collaborative Research: DMREF: Data-Driven Prediction of Hybrid Organic-Inorganic Structures

Lead Investigator: Hendrik Heinz, hendrik.heinz@colorado.edu
Participating Institutions: University of Colorado Boulder, Duke University, New Mexico Highlands University)
Source of Support: NSF-DMREF 2323546, 2323547, and 2323548
Website: https://bionanostructures.com/dmref-hois/
Keywords: AFRL, perovskite synthesis, crystal structure, molecular dynamics, machine learning

Project Scope

The goal of this project, in collaboration with AFRL, is to accelerate the structure prediction of hybrid organic inorganic structures (HOIS) of metal-halide perovskites from the starting materials through exploitation of recently curated X-ray structure databases with 1000+ HOIS (e.g., HybriD^3), molecular dynamics (MD) simulation, machine learning (ML), synthetic and structural studies in an iterative feedback loop. We will employ high-throughput MD simulations with the INTERFACE force field (IFF) to elucidate composition-structure relationships, including preferred dimensionality, distortions in the inorganic lattice, and relative stabilities. The targeted structures of metal-halide perovskites encode optical and electronic properties for applications in solar cells and LEDs.

Relevance to MGI

The team combines expertise in cutting-edge organic synthesis (**Marder**), perovskite synthesis and characterization (**Mitzi**), simulation and ML (**Heinz**), as well as inorganic material synthesis and characterization lead by minority researcher (**Castañeda**) and an MSI. Integration follows an iterative loop of developing and applying ML methods with physics-based input from materials science, chemistry, experimental and computational data, as well as workflows that provide mutual critique and suggestions for improvement. For example, full analysis of the HybriD^3 and other available databases aids in identifying HOIS crystal structure types, structure predictions by MD simulation and ML pipelines will be tested by laboratory synthesis and crystallography, IFF parameters and ML algorithms will be improved upon feedback, and new data will be added into open-source databases. The integration of these activities is necessary to utilize data and experimental/computational knowledge effectively, with up to 100 times acceleration in discovery of new HOIS with desirable stable structures, relative to serial discovery without MGI-style integration.

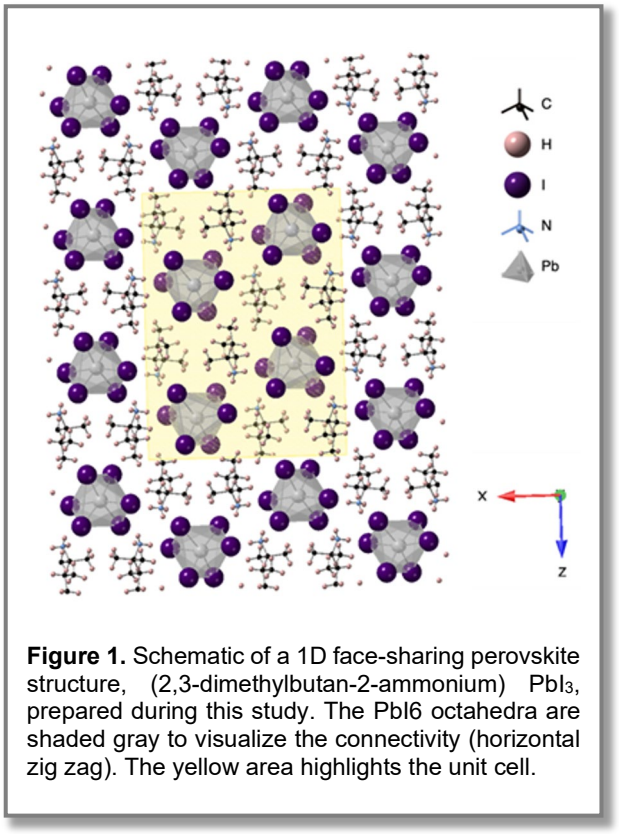


Figure 1. Schematic of a 1D face-sharing perovskite structure, (2,3-dimethylbutan-2-ammonium) PbI_3, prepared during this study. The PbI6 octahedra are shaded gray to visualize the connectivity (horizontal zig zag). The yellow area highlights the unit cell.

Technical Progress

The **Marder** team synthesized new organic cations to explore the impact of systematically varying the structure and monitoring their impact on the crystal structure of the corresponding metal halide hybrid phases (HOIS). A key series includes alpha-methylbenzylammonium salts ($XC_6H_4CHMeNH_3^+$) with varied halogens in various ring positions, including chiral hybrid phases with promising properties. Some organic cations have already been successfully incorporated into hybrid lead halide phases by the **Mitzi** group, and crystallization efforts are continuing. Several examples have also been sent to **Castañeda** to examine the impact of the cation structures on the crystal structures of the corresponding manganese(II) halides. The **Heinz** team has worked with Blum (collaborator, Duke U) and processed the entire HybriD^3 database with ~1,700 entries into ML-compatible format and derived correlations between structures and dimensionality, guided by **Mitzi** and **Marder**. ML models such as

gradient boosted trees (GBTs) can predict the dimensionality from the chemical formula with over 95% accuracy within fraction of a second, which is quite remarkable (manuscript in preparation). All PIs have begun to identify all unique structural types of perovskite-type HOIS for more detailed structure predictions (approximately 80 categories). Barriers towards usage for simulations and ML are being cleared, e.g., removing duplicates and processing incomplete entries in databases, correctly assigning elements and fractional occupancies into statistical distributions. Since <1000 unique structures in current databases are too small for predictive crystal structure assignments of new compositions into ~80 possible types, IFF MD simulations by **Heinz** and high-throughput experiments by Tod Grusenmeyer at AFRL will fill a critical gap in building a larger training dataset and model validation. **Heinz** has an extended visit to AFRL during summer to explore further collaborative synergies. Four publications from an earlier DMREF project on catalysis and other organic-inorganic structures have appeared.[1-4]

Future Plans

We will refine ~80 unique HOIS structure types using the complementary expertise of the team members, the Hybrid[3] database, and newly synthesized structures. The structure types will serve as the target of prediction for new synthetic combinations of organic and inorganic halides using MD simulation, AI and ML. We will define all structures with complete coordinate files, atomic charges, and atom types, ready for IFF MD simulations to allow combinatorial exchanges of organic and inorganic halide components via scripting for high-throughput screening of 1000+ candidates. MD simulations for initial sets of several hundred recent (**Mitzi**) and hypothetical HOIS will be carried out, and measures to rank the stability of each in the 80 possible structure types. Encouraging ML results by **Heinz** for the prediction of perovskite dimensionality from the composition using random forests and GBTs (which is easier than full structure type prediction) will be analyzed to explain how the models are learning from data. Processing of large datasets from spectroscopy that are soon expected from high-throughput synthesis and characterization at AFRL will be integrated. **Marder** will continue with organic synthesis to explore the range of chiral alpha-methylbenzylamine derivatives with two halo substituents on the phenyl ring and different groups in the alpha position (e.g., Et instead of Me). The **Mitzi** group plans to continue structural studies including changes in branching and connectivity of aliphatic cations, as well as changing stoichiometries of organic cations to halide components and connect with the **Heinz** team to use the systems as test cases for computational structure prediction. **Castañeda** will analyze impacts of chirality on stability and organize student exchanges with the R1 institutions.

Broader Impacts and Workforce Development

Several new manuscripts are in progress and the PIs plan to present multiple talks on initial results at the 2024 Fall ACS and MRS meetings. Our team includes minority serving institutions (MSIs), namely New Mexico Highlands University, links to Fort Lewis College (**Marder**) and the South Big Data Hub (**Heinz**) to expand broadening participation. Several undergraduates and REU students are involved and two graduate students currently intern at NREL and AFRL. The PIs organize multiple symposia and panel discussions on perovskites and AI/ML for materials discovery at upcoming ACS and MRS meetings.

Data Management and Open Access

Results, metadata, and code will be shared in Supporting Information of publications, including crystal structure databases and code repositories, e.g., Cambridge structural database, IFF website,[5] GitHub, Zenodo, HuggingFace, HybriD3 database[6] using public licenses such as Apache 2.0. The data will be checked for proper documentation, coding standards, and interoperability for ML. We also utilize PI's websites to share further information.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Without the MGI approach, serial synthesis and characterization takes several weeks for each new compound, and characterization of the available space of billions of possible perovskite-like HOIS for solar and LED technology would be a time-consuming effort. Once the machinery of highly reliable MD simulations and automated analysis of the stability of various structure types is established, lead compounds can be identified in less than a few days, or even less than a day using supercomputing. The AI/ML models based on databases, augmented by IFF MD and further robotic experiments at AFRL, after training, are expected to speed up crystal type discovery from weeks to minutes. Early adopters and users of these techniques include national laboratories, companies, and academic groups. Ties to NREL, BASF, Exxon, Amazon, and other potential stakeholders are already established, and will be further developed during this project.

Publications and References

1. Y. Yang, J. Zhou, Z. Zhao, G. Sun, S. Moniri, C. Ophus, Y. Yang, Z. Wei, Y. Yuan, C. Zhu, Q. Sun, Q. Jia, H. Heinz, J. Ciston, P. Ercius, P. Sautet, Y. Huang, J. Miao, *Atomic-Scale Identification of the Active Sites of Nanocatalysts*. Nature Catalysis, in print (2024). DOI: 10.1038/s41929-024-01175-8.
2. M. Tavakol, J. Liu, S. E. Hoff, C. Zhu, H. Heinz, *Osteocalcin: Promoter or Inhibitor of Hydroxyapatite Growth?* Langmuir, **40**, 1747 (2024). DOI: 10.1021/acs.langmuir.3c02948.
3. J. J. Winetrout, K. Kanhaiya, G. Sachdeva, R. Pandey, B. Damirchi, A. Van Duin, G. M. Odegard, H. Heinz, *Implementing Reactivity in Molecular Dynamics Simulations with Harmonic Force Fields*, Nature Comm., accepted (2024).
4. J. Huang, B. Peng, C. Zhu, M. Xu, Z. Liu, X. Duan, H. Heinz, Y. Huang, *Surface Molecular Pump Enables Ultrahigh Catalyst Activity*, Sci. Adv., accepted (2024).
5. H. Heinz, *Interface Force Field (IFF) and a Surface Model Database*. https://bionanostructures.com/interface-md/. 2013-2024.
6. V. Blum, *HybriD³ Materials Database*. https://materials.hybrid3.duke.edu/, 2024.

Machine Learning Algorithm Prediction and Synthesis of Next Generation Superhard Functional Materials

Lead Investigator: Russell J. Hemley, rhemley@uic.edu; Sara Kadkhodaei, sarakad@uic.edu; Ravhi Kumar, ravhi@uic.edu; Michael Trenary, mtrenary@uic.edu; Eva Zurek, ezurek@buffalo.edu; Gary Cook, gary.cook.9@us.af.mil

Participating Institutions: University of Illinois Chicago, University at Buffalo, AFRL/RYDH, PARADIM
Source of Support: NSF DMREF: DMR 2119065, DMR-2119308
Website: https://dmref.org/projects/1580
Keywords: High pressure, diamond-anvil cells, surface science, machine learning, density-functional theory

Project Scope

The goal of this project is to develop novel first-principles and machine-learning based computational tools and apply them towards the discovery of novel functional materials. These techniques are employed to guide both solid state high pressure and surface science methods to synthesize promising systems, whose properties are investigated. Students are being trained in an interdisciplinary collaborative team of theoreticians and experimentalists with expertise in chemistry, physics, materials science and engineering.

Relevance to MGI

Consistent with the MGI strategic plan, the project integrates experiment, computation, and theory in an iterative feedback loop among project tasks. The project is accelerating materials discovery and development of next generation functional superhard materials, as demonstrated by results from the past year, specifically in carbon- and boron-containing materials.

Technical Progress

We developed a novel 3D voxel representation of materials, using visual images to encode crystalline materials and deep CNNs to learn synthesis feasibility[1] and predict formation energy accurately[2]. We are among the first to demonstrate that the underlying physicochemical information of materials can be learned solely from their visual representation. This finding opens new possibilities for fully leveraging the power of machine learning in materials research. Additionally, the effect of data bias (data heterogeneity) on machine learning performance has been studied[3].

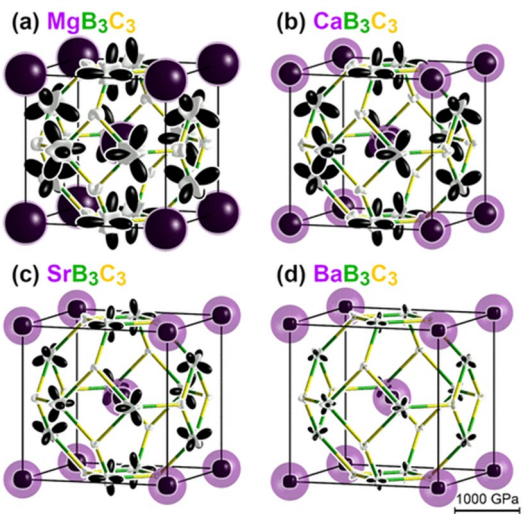


Figure. Chemical pressure (CP) schemes of simple B − C clathrates in the bipartite sodalite $Pm\bar{3}n$ structure at ambient pressure: (a) MgB_3C_3, (b) CaB_3C_3, (c) SrB_3C_3, and (d) BaB_3C_3. The large pressures present in MgB_3C_3 explain why it is dynamically unstable. Metal atoms are denoted in purple, and B/C atoms emanate green/yellow stick bonds. *JACS* **145**, 1696 (2023).

Joint high-pressure experiments and DFT calculations were utilized to study the resiliency, morphology, and transformations of a novel one-dimensional high-entropy oxide.[4] Extending our previous work on WB_2,[5] x-ray diffraction and spectroscopy reveal significant bonding changes in $BC_{3.3}N$ and B_4C on compression. A combined theoretical and experimental study with PARADIM MIP of B_4C has uncovered the origin of its well-known pressure-induced amorphization.

The ultrahigh thermal conductivity material BAs examined to megabar (183 GPa) was found to undergo pressure-induced amorphization in contrast to the previous transition report, with laser heating utilized to examine kinetically hindered phase transitions or decomposition leading to amorphization. A new study of FeV under pressure reveals the origin of its thermally frustrated phase transition under pressure.[6]

These joint theory-experiment high-pressure studies were extended to include related topological and strongly correlated materials during the past year. The band gap and compressibility of the novel chiral

semiconductor Ag_3AuTe_2 was examined using a broad range of experimental techniques,[7] a high-temperature concomitant metal-insulator and spin-reorientation transitions were discovered in the compressed nodal-line ferrimagnet $Mn_3Si_2Te_6$,[8] pressure tuning of competing interactions on a honeycomb lattice $Ag_3LiRh_2O_6$ was elucidated,[9] and a structural transition and uranium valence change in UTe_2 at high pressure were revealed by x-ray diffraction and spectroscopy.[10]

DFT calculations predicted C[11] and C/B-based[12] compounds that were metallic and stable at 1 atm. The superconducting critical temperature (T_c) of these materials was estimated using first-principles methods, and an ML model for sheer moduli was employed in conjunction with an analytical formula to estimate their Vickers hardness (H_v). The T_c of $KPbB_6C_6$ was predicted to be as high as 88 K, with an H_v of ~20 GPa.[12] The XtalOpt evolutionary algorithm was extended so that it can be employed to predict metastable structures with multiple functionalities[13] and interfaced with Kadkhodaei's ML model for synthesizability (XIE-SPP).

Fundamental surface science experiments were conducted to explore the chemistry associated with the growth of diboride thin films by chemical vapor deposition. Experimental results on the adsorption and decomposition of $Zr(BH_4)_4$ on a Pd(111) surface obtained by the Trenary group were interpreted with the aid of extensive computational work by the Zurek group.[14] Similar experimental-theoretical collaborative work is continuing on the homoepitaxial growth of ZrB_2 on a $ZrB_2(0001)$ single-crystal surface using $Zr(BH_4)_4$. These latter experimental studies including atomic-scale investigations with scanning tunneling microscopy (STM). To obtain clean well-ordered surfaces for STM studies of diborides requires heating them to temperatures as high as 2,000°C. To achieve this, a novel new sample heater was developed.[15]

Future Plans

Recent advances in large language models (e.g., GPT and Llama) present unprecedented opportunities to harness the vast amount of data that will be utilized to extract and tabulate chemical vapor deposition synthesis data for graphene and other 2D materials. This data will serve as the training set for our ML models, designed to guide synthesis recipes for 2D material growth. The multi-objective crystal structure search implemented within XtalOpt[13] will be applied to predict multi-functional metastable materials that have a high likelihood of synthesizability, as predicted with XIE-SPP. Theoretical calculations will be further performed to understand the significance of high pressure in phase transformation and amorphization in boron carbides. We will carry out high-*P*-*T* Raman spectroscopy to identify the phonons contributing to the ultrahigh thermal conductivity of BAs.

Broader Impacts and Workforce Development

Educational Outreach. In collaboration with Oakton Community College, Kadkhodaei and her team presented hands-on learning activities in the 2023 Futures Unlimited workshop, targeting 800+ middle-school girls and gender-expansive students and exposing them to materials science and engineering fields. Zurek gave a lecture and hands-on tutorial at the 8th Annual JHU Summer School "Data Driven Materials Discovery: From ML to Maker Space" organized by the PARADIM MIP. Hemley has featured this work in public lectures at UIC and continues to work with PARADIM MIP. Workforce Development. Kadkhodaei's lab has trained 3 PhD students and 2 undergraduate students with the support of this project. One of the PhD students graduated in December 2023, with his dissertation being fully supported by this grant. Zurek has trained 2 PhD students and 2 postdocs supported by this grant. Trenary has graduated 2 PhD students and has 2 current PhD students supported by this grant. Hemley has supported 3 PhD students and 1 postdoc under this grant, and 3 undergraduates have worked on projects, leveraging DoD NDEP funding,

Data Management and Open Access

Machine learning codes and data are published as an accessible software toolkit with detailed instructions for installation, usage, and examples[16] (https://github.com/kadkhodaei-research-group/XIE-SPP). The developments within XtalOpt have been made available in Release 13.0 (https://xtalopt.github.io) and will be deposited in the Computer Physics Communications library as part of our recently accepted publication[13]). The outputs of the computations are uploaded to repositories including NOMAD (https://nomad-lab.edu)

Advancing Along the Materials Development Continuum and Partnerships to Translation

Patent disclosures on related superconducting materials have been filed through UIC.

Publications and References

1. Davariashtiyani, A.; Kadkhodaie, Z.; Kadkhodaei, S., Predicting synthesizability of crystalline materials via deep learning. *Commun. Mater.* **2021,** *2* (1), 115.
2. Davariashtiyani, A.; Kadkhodaei, S., Formation energy prediction of crystalline compounds using deep convolutional network learning on voxel image representation. *Commun. Mater.* **2023,** *4* (1), 105.
3. Davariashtiyani, A.; Wang, B.; Hajinazar, S.; Zurek, E.; Kadkhodaei, S., Impact of Data Bias on Machine Learning for Crystal Compound Synthesizability Predictions, Machine Learning: Science and Technology (Submitted, Under review). *https://arxiv.org/abs/2406.17956*.
4. Shahbazi, H.; Seraji, P.; Faraj, H.; Yang, T.; Kim, A.; Fattahpour, S.; Papailias, I.; Diamond, M.; Namvar, S.; Ahmadiparidari, A.; Wang, S.; Liu, Z.; Kumar, K.; Aihaiti, M.; Cabana, J.; Kadkhodaei, S.; Wang, J.; Huang, Z.; Hemley, R. J.; Salehi-khojin, A., Resiliency, Morphology, and Transformations of a One-Dimensional High-Entropy Oxide. *Nature Comm., submitted.*
5. Lim, J.; Hire, A. C.; Quan, Y.; Kim, J. S.; Xie, S. R.; Sinha, S.; Kumar, R. S.; Popov, D.; Park, C.; Hemley, R. J.; Vohra, Y. K.; Hamlin, J. J.; Hennig, R. G.; Hirschfeld, P. J.; Stewart, G. R., Creating superconductivity in WB_2 through pressure-induced metastable planar defects. *Nature Commun.* **2022,** *13* (1), 7901.
6. Pulido, H. R.; Bimal, K. C.; Kumar, R.; Hemley, R. J.; Muñoz, J. A., Thermally frustrated phase transition at high pressure in B2-ordered FeV. *AIP Adv., in press*.
7. Won, J.; Zhang, R.; Peng, C.; Kumar, R.; Gebre, M. S.; Popov, D.; Hemley, R. J.; Bradlyn, B.; Devereaux, T.; Shoemaker, D. P., Band gap and compressibility of Ag_3AuTe_2. *Phys. Rev. B, submitted*.
8. Susilo, R. A.; Kwon, C. I.; Lee, Y.; Salke, N. P.; De, C.; Seo, J.; Kang, B.; Hemley, R. J.; Dalladay-Simpson, P.; Wang, Z.; Kim, D. Y.; Kim, K.; Cheong, S.-W.; Yeom, H. W.; Kim, K. H.; Kim, J. S., Publisher Correction: High-temperature concomitant metal-insulator and spin-reorientation transitions in a compressed nodal-line ferrimagnet Mn3Si2Te6. *Nature Commun.* **2024,** *15* (1), 5269.
9. Sakrikar, P.; Shen, B.; Poldi, E. D. T.; Bahrami, F.; Hu, X.; Kenney, E. M.; Wang, Q.; Fruhling, K. W.; Wang, C.; Gupta, R.; Khasanov, R.; Luetkens, H.; Calder, S. A.; Aczel, A. A.; Fabbris, G.; Hemley, R. J.; Plumb, K. W.; Ran, Y.; Gegenwart, P.; Tsirlin, A. A.; Haskel, D.; Graf, M. J.; F. Tafti, Pressure tuning of competing interactions on a honeycomb lattice. *Nature Commun., in press*.
10. Deng, Y.; Lee-Wong, E.; Moir, C. M.; Kumar, R. S.; Swedan, N.; Park, C.; Popov, D.; Xiao, Y.; Chow, P.; Baumbach, R. E.; Hemley, R. J.; Maple, M. B., Structural transition and uranium valence change in UTe_2 at high pressure revealed by x-ray diffraction and spectroscopy. *Phys. Rev. B, in press*.
11. Wang, X.; Proserpio, D. M.; Oses, C.; Toher, C.; Curtarolo, S.; Zurek, E., The Microscopic Diamond Anvil Cell: Stabilization of Superhard, Superconducting Carbon Allotropes at Ambient Pressure. *Angew. Chem. Int. Ed.* **2022,** *61* (32), e202205129.
12. Geng, N.; Hilleke, K. P.; Zhu, L.; Wang, X.; Strobel, T. A.; Zurek, E., Conventional High-Temperature Superconductivity in Metallic, Covalently Bonded, Binary-Guest C–B Clathrates. *J. Am. Chem. Soc.* **2023,** *145* (3), 1696-1706.
13. Hajinazar, S.; Zurek, E., XtalOpt Version 13: Multi-Objective Evolutionary Search for Novel Functional Materials. . *Comput. Phys. Commun. Accepted (2024), arXiv:2405.02138*.
14. Ranjan, R.; Redington, M.; Ologun, A.; Zurek, E.; Miller, D. P.; Trenary, M., Identification of a Stable B2H2 Intermediate in the Decomposition of Zr(BH4)4 on the Pd(111) Surface. *J. Phys. Chem. C, (2024). Under review, submitted 4/9/2024; Revisions submitted 6/19/2024*.
15. Gedara, B. S. A.; Trenary, M., Heating samples to 2000 °C and above for scanning tunneling microscopy studies in ultrahigh vacuum. *J. Vac. Sci. Technol. B* **2024,** *42* (1) 014201.
16. Davariashtiyani, A., XIE-SPP: Crystal Image Encoder for Synthesis & Property Prediction *Github, https://github.com/kadkhodaei-research-group/XIE-SPP*.

DMREF AI-Accelerated Design of Synthesis Routes for Metastable Materials

Lead Investigator: Richard G. Hennig, rhennig@ufl.edu
Participating Institutions: University of Florida
Source of Support: NSF-DMREF 2118718.
Website: https://super.mse.ufl.edu
Keywords: Metastable materials, deep learning, ultra-fast force fields, superconductivity, magnetism, hardness.

Project Scope

The project addresses the science of nonequilibrium processes by searching for and identifying the design rules for synthesis pathways of metastable materials. We combine computational methods, including AI, with experimental approaches utilizing pressure, temperature, and magnetic fields to transform amorphous precursor materials into desired phases that are kinetically stable at ambient conditions and persist indefinitely at ambient conditions. We will build the fundamental knowledge base to discover and design materials that exhibit unusual compositions and structures, are inaccessible to synthesis processes at ambient pressure and provide desirable properties and functionality for applications such as superconductivity, magnetism, and superhardness.

Relevance to MGI

Our design approach is based on a closed loop combining AI for structure prediction and ab-initio methods for calculating properties with high pressure, magnetic field, and temperature synthesis and characterization. We develop computational methods that employ deep learning to predict materials structures with optimal properties and the ultra-fast force field machine learning of energy landscapes to model the finite temperature and pressure thermodynamics and kinetic stability of both crystalline and amorphous phases. The design process identifies experimental conditions that stabilize desired high-pressure and temperature phases at ambient conditions in metastable form. Experimental synthesis and characterization validate and guide the approach, leading to new synthesis pathways. Products will include new metastable synthesis methods, machine learning approaches for structure prediction and characterization of their thermodynamics and kinetics, and metastable materials with a wide variety of desirable properties such as superconductivity, magnetism, and superhardness.

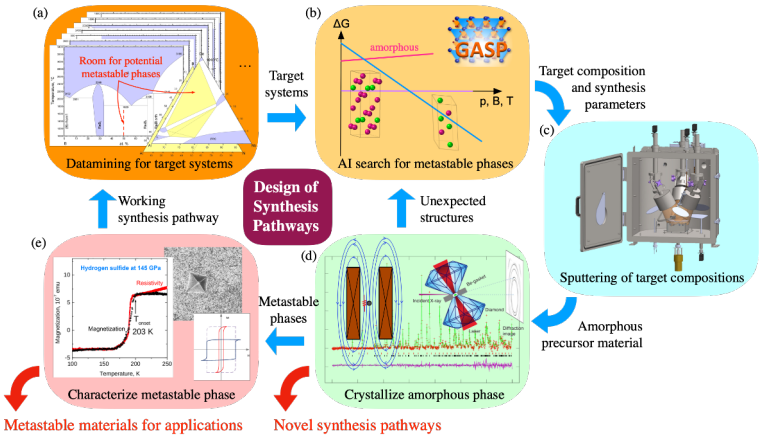


Figure 1. Schematic representation of the proposed flow of activities.

Technical Progress

In the first three years of the project, we (i) developed the ultra-fast force field (UF^3) method for energy landscapes and implemented it into the LAMMPS package to enable exascale simulations of materials, (ii) trained a bootstrapped ensemble of tempered equivariant graph neural networks on the electron-phonon spectral function of materials to predict new superconducting compounds, (iii) designed, built, and applied a tool for rapidly quenching liquids to synthesize metastable amorphous and crystalline materials, (iv) refined and tested the high-magnetic field furnace to anneal amorphous materials in high fields, and (v) applied our rapid quenching and high-pressure approaches to synthesize metastable superconducting borides and identified a new mechanism for creating superconductivity in materials through filamentary defects.

AI methodology. Integrating deep learning with the search for new electron-phonon superconductors represents a burgeoning field of research, where the primary challenge lies in the computational intensity of calculating the electron-phonon spectral function, $\alpha^2F(\omega)$, the essential ingredient of Midgal-Eliashberg theory of superconductivity. To overcome this challenge, we adopted a two-step approach. First, we computed $\alpha^2F(\omega)$ for 818 dynamically stable materials. We then trained a deep-learning model to predict $\alpha^2F(\omega)$, using an unconventional

training strategy to temper the model's overfitting, enhancing predictions. Specifically, we trained a Bootstrapped Ensemble of Tempered Equivariant graph neural NETworks (BETE-NET). Further, we incorporate domain knowledge of the site-projected phonon density of states to impose inductive bias into the model's node attributes and enhance predictions. This methodological innovation yields a mean absolute error of 2.1 K for T_c. We applied the model to a high-throughput screening for high-T_c materials. The model demonstrates an average precision nearly five times higher than random screening, highlighting the potential of ML in accelerating superconductor discovery. BETE-NET accelerates the search for high-T_c superconductors while setting a precedent for applying ML in materials discovery, particularly when data is limited.

Ab-initio studies. Recently, the team's attention was drawn to an exciting discovery of 80K superconductivity in the new $La_3Ni_2O_7$ nickelate material. Since superconductivity in $La_3Ni_2O_7$ takes place only above 20 GPa of applied pressure, we performed extensive simulations of the crystal and electronic structures of this material and a wide range of substitutions on the rare earth site, making predictions for promising new superconductors. We also investigated optical properties to determine the level of electronic correlation.

Experimental synthesis. We investigate a broad range of synthesis conditions (temperature, pressure, and magnetic fields) for the predicted materials. Utilizing the splat cooler developed in this project, we rapidly quench materials from the liquid phase to room temperature. Subsequent annealing in zero magnetic field and with our high-magnetic field furnace at fields of 9 T at temperatures up to 1500 K provides insight into the kinetic stability of amorphous and crystalline structures. Through the application of pressure in diamond anvil cells, we had previously demonstrated that the high-pressure synthesis of metastable planar defect phases during compression of WB_2 presents a novel mechanism for filamentary superconductivity. We extended our study to MoB_2 and showed that alloying sufficiently increases the stability of the metastable, superconducting AlB_2 phase at ambient pressure. We confirmed the formation of the planar defect phases using aberration-corrected scanning tunneling electron microscopy in collaboration with the group of Prof. Honggyu Kim at the University of Florida.

Future Plans

To further enhance our AI-driven prediction of new crystalline materials, we will combine BETE-Net and our UF3 machine-learning potentials with other AI tools to build an optimized workflow for superconductors. First, to improve the prediction accuracy of BETE-Net about three-fold, we will increase the number of electron-phonon spectral functions for training from 818 to about 10,000. Second, to move beyond known crystal structures, we will develop a generative model and utilize the spectral functions as context to guide the model in predicting new crystalline materials with a high probability of superconductivity.

To predict the stability of stable and metastable crystalline and amorphous phases and help identify optimal synthesis pathways, we will train UF^3 models on density-functional relaxations and simulate various synthesis conditions as a function of temperature, composition, and pressure. In parallel, we will synthesize, quench, pressurize, and anneal amorphous and crystalline precursor phases in these systems to tune the experimental conditions and validate our predictions. The results will be used to identify further promising material systems, identify novel synthesis conditions, and help explain experimental observations.

Broader Impacts and Workforce Development

PI Hennig has developed and twice taught a new undergraduate and graduate course on *AI for Materials*. The next step is to integrate the course into the MSE undergraduate curriculum as a required course. In addition to the software tools for machine learning, PI Hennig this year developed Jupyter notebooks for teaching fundamental thermodynamics concepts. We freely provide our educational material and Jupyter notebooks to other teachers, students, and the interested general public through our GitHub organization for Materials Education at https://github.com/matscied. We plan to expand this effort and also provide additional teaching material. In the following years, we will also develop an experiment kit for K-12 use that demonstrates synthesis methods and make this kit available to teachers across the southeastern states, Puerto Rico, and the US Virgin Islands. Through our partnership with the education program of Prof. Ruzycki, we will train teachers in its use and refine the module based on feedback.

Data Management and Open Access

We freely provide all software and documentation on our Github page https://github.com/henniggroup. Furthermore, all datasets are made available on sites such as https://www.materialscloud.org, and synthesis recipes are published through peer-reviewed manuscripts.

Publications and References

1. J. Lim, A. C. Hire, Y. Quan, J. S. Kim, S. R. Xie, S. Sinha, R. S. Kumar, D. Popov, C. Park, R. J. Hemley, Y. K. Vohra, J. J. Hamlin, R. G. Hennig, P. J. Hirschfeld, and G. R. Stewart, *Creating superconductivity in WB_2 through pressure-induced metastable planar defects*, Nat. Communications **13**, 7901 (2022), https://doi.org/10.1038/s41467-022-35191-8.
2. T. A. Elmslie, D. VanGennep, R. N. Baten, J. Downing, W. Bi, S. T. Weir, Y. K. Vohra, R. E. Baumbach, and J. J. Hamlin, Pressure-induced superconductivity in the weak topological insulator Bi_2TeI and the topological metal Bi_3TeI. arXiv:2209.02688 (2022), https://doi.org/10.48550/arXiv.2209.02688.
3. A. C. Hire, S. Sinha, J. Lim, J. S. Kim, L. Fanfarillo, P. M. Dee, J. J. Hamlin, R. G. Hennig, P. J. Hirschfeld, G. R. Stewart, *High Critical Field Superconductivity at Ambient Pressure in MoB_2 Stabilized in the P6/mmm Structure via Nb Substitution*, Phys. Rev. B 106, 174515 (2022), https://doi.org/10.1103/PhysRevB.106.174515.
4. J. Lim, S. Sinha, A. C. Hire, J. S. Kim, P. M. Dee, R. S. Kumar, D. Popov, R. J. Hemley, R. G. Hennig, P. J. Hirschfeld, G. R. Stewart, and J. J. Hamlin, *Niobium substitution suppresses the superconducting critical temperature of pressurized MoB_2.* Phys. Rev. B 108, 094501 (2023), https://doi.org/10.1103/PhysRevB.108.094501.
5. S. R. Xie, M. Rupp, R. G. Hennig, *Ultra-fast interpretable machine-learning potentials*, npj Computational Materials 9, 162 (2023), https://doi.org/10.1038/s41524-023-01092-7.
6. A. Sahinovic, B. Geisler, R. Pentcheva, *Nature of the magnetic coupling in infinite-layer nickelates versus cuprates*. Phys. Rev. Materials 7, 114803 (2023), https://doi.org/10.1103/PhysRevMaterials.7.114803.
7. B. Geisler, *Rashba spin-orbit coupling in infinite-layer nickelate films on SrTiO3(001) and KTaO3(001).* Physical Review B **108**, 224502 (2023), https://doi.org/10.1103/PhysRevB.108.224502.
8. P. M. Dee, J. S. Kim, A. C. Hire, J. Lim, L. Fanfarillo, S. Sinha, J. J. Hamlin, R. G. Hennig, P. J. Hirschfeld, G. R. Stewart, *Diboride compounds doped with transition metals: A route to superconductivity through structure stabilization as well as defects*. Physical Review B 109, 104520 (2024), https://doi.org/10.1103/PhysRevB.109.104520.
9. B. Geisler, J. J. Hamlin, G. R. Stewart, R. G. Hennig, and P. J. Hirschfeld, *Structural transitions, octahedral rotations, and electronic properties of $A_3Ni_2O_7$ rare-earth nickelates under high pressure*. npj Quantum Materials 9, 38 (2024), https://doi.org/10.1038/s41535-024-00648-0.
10. B. Geisler, L. Fanfarillo, J. J. Hamlin, G. R. Stewart, R. G. Hennig, and P. J. Hirschfeld, *Optical properties and electronic correlations in $La_3Ni_2O_7$ bilayer nickelates under high pressure*. arXiv:2401.04258 (2024), https://doi.org/10.48550/arXiv.2401.04258.
13. J. B. Gibson, A. C. Hire, P. M. Dee, O. Barrera, B. Geisler, P. J. Hirschfeld, and R. G. Hennig, *Accelerating superconductor discovery through tempered deep learning of the electron-phonon spectral function*. npj Computational Materials, under review (2024), https://doi.org/10.48550/arXiv.2401.16611.
14. Y. Deng, F. Taraporevala, H. Wang, E. Lee-Wong, C. M. Moir, J. Lim, S. Sinha, W. Xie, J. J. Hamlin, Y. Vohra, and M. B. Maple, Pressure induced metallization and loss of surface magnetism in FeSi, arXiv:2405.04739 (2024), https://doi.org/10.48550/arXiv.2405.04739.

DMREF: Accelerated Design, Discovery, and Deployment of Electronic Phase Transitions (ADEPT)

Lead Investigator: Christopher Hinkle, University of Notre Dame, chinkle@nd.edu
Participating Institutions: Divine Kumah (Duke University), Suman Datta (Georgia Tech), Wei Chen and James Rondinelli (Northwestern University)
Source of Support: NSF-DMREF #2324172
Website: none yet
Keywords: insulator-metal transition, correlated oxide, cross-point selector, embedded non-volatile memory

Project Scope
The ADEPT project aims to implement an accelerated discovery and codesign engine for efficient design and discovery of materials exhibiting insulator-metal transitions (IMTs) that display large changes in the electrical resistivity for selector devices and RF switches. Achieving this goal requires moving beyond conventional, linear approaches to materials discovery, transforming them into a cyclic and iterative process. The project formulates new computational approaches that fuse computational data with high-throughput materials synthesis and characterization data to overcome key challenges of (*i*) Materials Discovery from Sparse & Expensive Data, (*ii*) Efficient Decoding of High-Dimensional Data, and (*iii*) Property-Performance Mismatch upon Integration.

Relevance to MGI
This interdisciplinary DMREF will employ a synergistically "closed loop" framework integrating computation, experiment, and theory to formulate the processing-structure-property-performance relationships necessary to advance IMT materials and devices (selectors, RF switches, RF limiters). This includes developing adaptive learning and autonomous methods for simulation and high-throughput synthesis and characterization and generating and distributing data through novel cyber-physical systems. Manufacturability is prioritized by implementing a codesign approach to account for process-property relationships that affect the performance of designed materials in scaled device structures during operation. We leverage industrial partnerships and recent cyberinfrastructure developed by Chen and Rondinelli, including new open-source ML techniques using natural language processing, conditional variational autoencoders, active learning, and LVGP integrated with Bayesian optimization.

Technical Progress
The Rondinelli and Chen groups have advanced AI-virtual screening and adaptive discovery for new single and two-phase IMT materials. Using an ML classification model, we screened a high-throughput crystal structure database and performed chemical substitutions to identify a novel Ca_2MoO_4 compound with a potential thermally driven transition. This compound is isostructural to Ca_2RuO_4, where changes in effective correlation strength drive a structural phase transition that opens the electronic band gap. Our density functional theory studies indicate that this transition occurs due to the distortion of metal-oxygen octahedra, resulting in the splitting of the 3 t_{2g} states to produce half-occupied states with the Mott transition opening a bandgap, thus creating an insulator. We have also created initial models of digital two-phase systems, focusing on the electronic structures of Ti_2O_3 and $MnTiO_3$ synthesized by Kumah and characterized by Hinkle, and their superlattice. After calibrating the DFT models with experimentally measured bandgaps of both compounds, we performed slab calculations to determine the band alignment at the interface and assess potential charge transfer. The system comprises Ti^{3+}, Ti^{4+}, and d^5 Mn^{2+}. We hypothesize that controlling the Ti redox reaction through interface density will allow tuning of the critical temperature, which will be tested in future studies. Kumah has identified relevant synthesis parameters to input into machine learning models to accelerate the identification of films with optimized metal-insulator transitions under ambient conditions in the TiOx family. A series of films have been synthesized by molecular beam epitaxy with varied growth rates, oxygen partial pressures, and substrate temperatures. Crystal structures have been

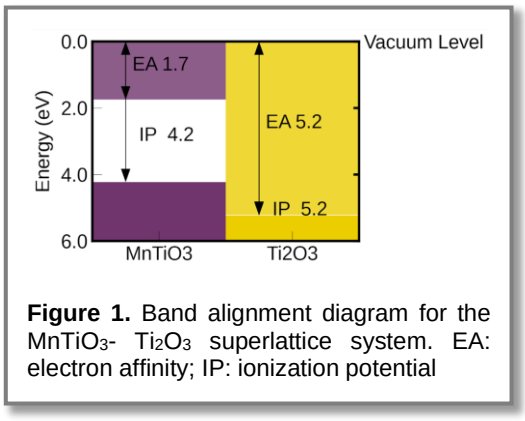


Figure 1. Band alignment diagram for the $MnTiO_3$- Ti_2O_3 superlattice system. EA: electron affinity; IP: ionization potential

characterized by X-ray diffraction, and a database has been constructed to serve as training data for the machine learning models. Hinkle has developed deep learning analysis of diffraction and XPS data to accelerate characterization of these films and provide data for Chen for adaptive learning experiment design. Datta has demonstrated a two-terminal bi-directional selector for cross-point embedded non-volatile memory applications using the high-temperature spin-state driven IMT phase transition in $LaCoO_3$ (LCO). The vertical selectors were fabricated using epitaxial heterostructures with LCO thin films grown on $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) bottom electrodes. Key findings include: (1) Electrically triggered abrupt IMT, (2) Operation across a wide temperature range (>85 °C), (3) Fast switching speeds (<20 ns), high on-current density (5×10^6 A/cm^2), and substantial half-bias nonlinearity (135×), and (4) Excellent endurance, exceeding 10^{12} cycles.

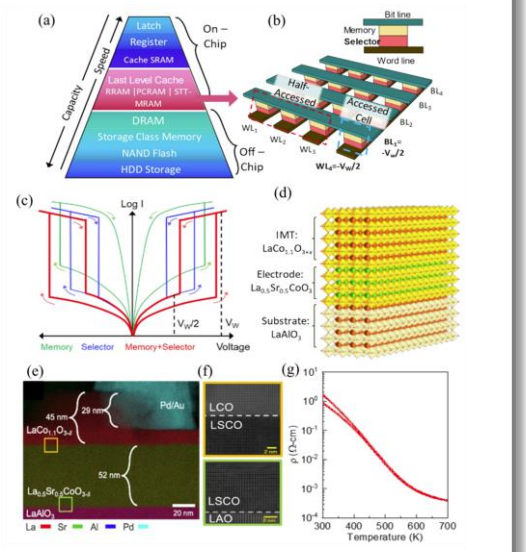


Figure 2. Schematic, images of epitaxial films, and switching characteristics of LCO-based IMT selectors.

Future Plans

Rondinelli and Chen will continue studying the IMT in Ca_2MoO_4, focusing on changes in the d orbital structure, building a regression model to predict its critical temperature, and working with Hinkle and Kumah to understand strain effects and synthesis conditions. For the $Ti_2O_3/MnTiO_3$ superlattices, we will model epitaxially grown superlattices with larger periodicities and begin constructing surrogate models to predict IMT behavior using symbolic regression for Landau models and DFT energies. Initial synthesis has been completed on $Ti_2O_3/MnTiO_3$ superlattices based on the calculations. The effect of doping and interface interactions will be explored. Datta's future work involves enhancing the nonlinearity of selectors and evaluating the new IMTs made by the synthesis team.

Broader Impacts and Workforce Development

Rondinelli worked with the Physicists To-Go initiative of the American Physical Society through their Public Engagement office. The program goal aims to connect scientists and educators and bring the wonders of physics to K-12 and college classrooms worldwide as one way to increase student interest and prepare students for a future advanced workforce. Rondinelli partnered with Ms. Cheryl Harper, who teaches at Greensburg Salem High School that matriculates students with diverse ethnic and financial backgrounds. Rondinelli virtually visited with more than 25 junior and senior high school students to share his experience with materials physics, quantum science and technology, how his interests began, what he was like at the student's age, and other aspects of his journey to his current position. Students asked questions on material science, machine learning, and dark matter for 90 minutes. Hinkle participated as a speaker and panelist at an Inclusive Engineering Consortium Workshop on broadening opportunities in microelectronics for students at HBCUs and other Minority Serving Institutions.

Data Management and Open Access

A database summarizing the growth conditions and crystal properties is shared using Google Drive. The data generated during the synthesis and associated metadata (Reflection high energy electron diffraction image files, growth scripts) are stored in a sharable Google Drive location online. The code for the PRX Energy publication (see below) is available: https://github.com/Henrium/MolSets. The dataset from the paper is also provided there.

Publications

1. Y-C. Luo, A. Khanna, B. Grisafe, J. Sun, S. Dutta, L. E. Noskin, C. Adamo, A. B. Mei, R. Ghosh, M. Colletta, M. E. Holtz, V. Gambin, L. F. Kourkoutis, S. Yu, D. G. Schlom, and S. Datta, *Correlated Oxide Selector for Cross-Point Embedded Non-Volatile Memory*, IEEE Transactions on Electron Devices **71**, 916 (2024). DOI: 10.1109/TED.2023.3338184.

2. H. Zhang, T. Lai, J. Chen, A. Manthiram, J.M. Rondinelli and W. Chen, *Learning Molecular Mixture Property Using Chemistry-Aware Graph Neural Network*, PRX Energy **3**, 023006 (2024). DOI: 10.1103/PRXEnergy.3.023006 (This includes a press release: https://www.mccormick.northwestern.edu/news/articles/2024/06/ai-algorithm-identifies-high-performing-electrolytes-for-batteries/

Designing Covalent Organic Frameworks for membrane separations and functionalized graphene with exact pore sizes

Lead Investigator: John Hoberg, hoberg@uwyo.edu
Participating Institutions: University of Wyoming
Source of Support: NSF-DMREF
Website: none
Keywords: Functionalized graphene, Two-dimensional covalent organic frameworks, membrane separations

Project Scope

New materials based on covalent organic frameworks (COFs) with defined and modifiable pores make them naturally suited for a host of applications given their 2D nature. By putting charged functional groups in the pores and changing the pore sizes, new properties and applications such as ion selective membranes can be obtained. Our team consists of materials synthetic chemist, computational scientist and engineers to design these new materials. We use computational modeling with machine learning to guide the synthesis of the new materials and optimize their performance for a particular application.

Relevance to MGI

The research aligns with the goals of the DMREF Materials Genome Initiative to accelerate materials discovery and development by building the fundamental knowledge base needed to advance the design and development of COF materials with desirable properties and functionality. The modularity and corresponding extensive phase space of COFs makes them prime candidates for computer-aided, high-throughput, materials discovery and design. We use a machine learning-based approach to identify quantitative structure-property relationships (QSPR) to predict COF behavior. Through an automated computational screening of candidate frameworks, we will not just discover novel functional COFs, but learn how to reverse engineer frameworks for desired applications, starting with desalination. Our interwoven experimental and computational approach will guide the research towards solving some of the world's pressing issues related to clean water and energy.

Technical Progress

Functionalizing graphene with exact pore size, specific functional groups, and precision doping poses many significant challenges. Current methods lack precision and produces random pore sizes, site of attachments and amounts of dopant leading to compromised structural integrity and effecting graphene's applications. We have recently accomplished the synthesis of functionalized graphitic materials with modifiable nanometer sized pores via a Pictet-Spengler polymerization reaction, figure 1. This one-pot, four step synthesis produces crystalline two-dimensional materials that were confirmed by pXRD, TEM measurements and DFT studies. These new COF materials are structurally analogous to doped graphene and graphene oxide (GO) but unlike GO maintain their semi-conductive properties when fully functionalized. Furthermore, exact placement and amounts of both the nitrogen and oxygen's are achieved in the COF materials, whereas in graphene only random numbers and placement are possible. We have also constructed a highly ordered metal doped material from these COFs. The stacking motif of 2D-materials does effect membrane separation performance relative to rejection and solvent permeance. Thus to gain insight into the materials stacking details, density functional theory (DFT) was performed with the results of just two COFs depicted in Figure 2. The images show both top-down and side views

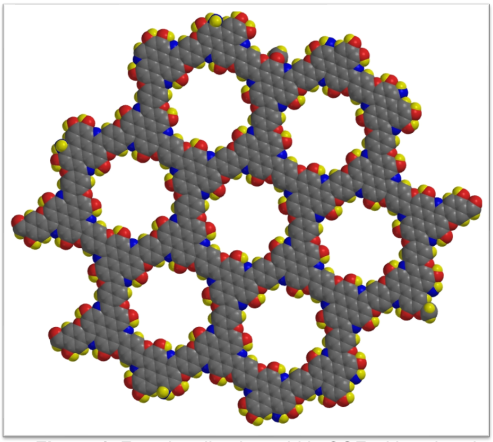


Figure 1. Functionalized graphitic COF with ordered pores "doped" with nitrogen and oxygen.

for the two different COF using three layers. The structures have been colored to show variations in height where red indicates higher positions and blue indicates lower positions. The layers of the smaller pore COF (top with pore size of 1.4 nm) are relatively planar while in the lower COF (pore size of 2.1 nm) they become wavy. The greater linker lengths and smaller pore functional group sizes (OH) lead to increased waviness in the 2D-COF geometries, as illustrated. This increase in pore size allows the PACs' nodes over a pore to sink down closer to the node in the alternating layer creating the wavy layering. As seen in both, the materials predominantly adopt an AB stacking geometry and along with the planarity greatly impact membrane separation performance.

We have also discovered two high impact defects that greatly affect separation performance. One is illustrated in figure 3 and is the first example of screw dislocation in a COF. A screw dislocation occurs when there is a linear defect within the atomic arrangement causing a growing layer to tilt vertically up or down such that as growth continues the lattice is distorted in a helical manner around a line axis, like a spiral staircase. The second defect we have discovered is a propensity for a 2D-COF to form hollow spheres during membrane formation. Both of these "defects" greatly impact membrane performance and are occurrences that have gone unreported in the COF/membrane literature.

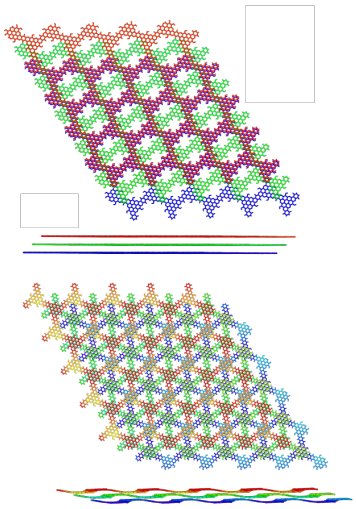


Figure 2. Computational models of graphitic COFs with different pore sizes.

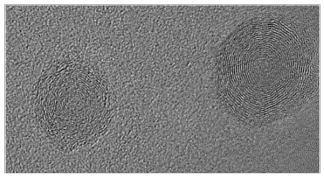


Figure 3. Screw dislocation in a COF.

Future Plans

Achieving the synthesis of the new graphitic COFs in figure 1 opens a door to new graphene type materials. As stated, these materials have precisely placed nitrogen and oxygen atoms in the carbon framework, have adjustable highly defined pore sizes that can be functionalized to fit a desired need. Thus, applications that have been developed and targeted by GO will be investigated in the future. These would include areas beyond separation such as semi-conductor devices, batteries, heterogenous catalysis etc.

Broader Impacts and Workforce Development

We have hired two post-doc research associates and four graduate students all of whom are mentors for seven undergraduate STEM students. Combined group meetings involve discussions and presentations of theorist, synthetic chemists and membrane engineers, which help to train the next generation in all aspects of this materials research. In each of these activities the MGI philosophies are accentuated to highlight the overlap and impact of both the theory and testing on guiding synthetic designs. Students involved in the project have presented their research to the outside community at the National ACS meeting and annual MRI conferences. During the summers of 2023 and 24, REU students have also been engaged in this research. All these students are included in the publications listed below.

Data Management and Open Access

To date, we have performed calculations using COFs from the CoRE COF and CURATED COF databases, and modeled COFs synthesized by our team. The results from both calculations (e.g., band structures, charge distribution) and the geometries from the latter set of COF calculations, have been reported in the literature, and are included into existing databases, such as the CoRE COF database (for COF geometries) or the Novel Materials Discovery (NoMaD) database (for electronic structure properties). Automation scripts for the machine learning component of the project have been saved on GitHub

Advancing Along the Materials Development Continuum and Partnerships to Translation

Multiple patent applications have been filed and we have created a new materials center at the University after obtaining $900,000 seed grant.

Publications and References

1. A. E. Davies, M. J. Wenzel, C. L. Brugger, J. Johnson, B. A. Parkinson, J. O. Hoberg, and L. de Sousa Oliveira, *Computationally directed manipulation of cross-linked covalent organic frameworks for membrane applications Phys. Chem. Chem. Phys.*, **25,** 31090 (2023). DOI: 10.1039/d3cp04452a

2. K. Coe-Sessions, A. E. Davies, B. Dhokale, M. J. Wenzel, M. M. Gahrouei, N. Vlastos, J. Klaassen, B. A. Parkinson, L. de Sousa Oliveira and J. O. Hoberg, *Functionalized graphene via a one pot reaction enabling exact pore sizes, modifiable pore functionalization and precision doping.* J. Am. Chem. Soc. under review.

3. B. Dhokale, K. Coe-Sessions, M. J. Wenzel, A. E. Davies, T. Kelsey, L. de Sousa Oliveira, B. A. Parkinson, and J. O. Hoberg, *Engineering screw dislocations in Covalent Organic Frameworks* . J. Am. Chem. Soc. under review.

4. M. J. Wenzel, A. E. Davies, B. A. Parkinson, L. de Sousa Oliveira and J. O. Hoberg, *Predicting unexpected side reactions within a covalent organic framework using computational methods* M. J. Wenzel, A. E. Davies, T. Kelsey, L. de Sousa Oliveira B. A. Parkinson, and J. O. Hoberg under revision for resubmission.

DMREF: Data-driven Recursive AI-powered Generator of Optimized Nanostructured Superalloys (DRAGONS)

Lead Investigator: Andrea M. Hodge, ahodge@usc.edu
Participating Institutions: University of Southern California, University of California Santa Barbara, Johns Hopkins University
Source of Support: NSF-DMREF
Website: none
Keywords: processing genome, magnetron sputtering, heterogeneous designs, multiscale modeling, data-driven testbed

Project Scope

The objective of this DMREF project is to leverage machine learning and data science to elucidate the processing-microstructure relationships in novel materials production, supporting a new frontier for the Materials Genome Initiative. The project will develop DRAGONS, a data-driven platform, to interpret and predict microstructure attributes based on processing conditions and vice versa. Focused on Ni-based superalloys, the research integrates high-throughput magnetron sputtering and heat treatment techniques. Success will be measured by the accuracy of DRAGONS in predicting microstructures, validated through iterative synthesis, characterization, atomistic simulation, and phase field modeling. This initiative aims to revolutionize alloy development and foster impactful educational programs in materials engineering.

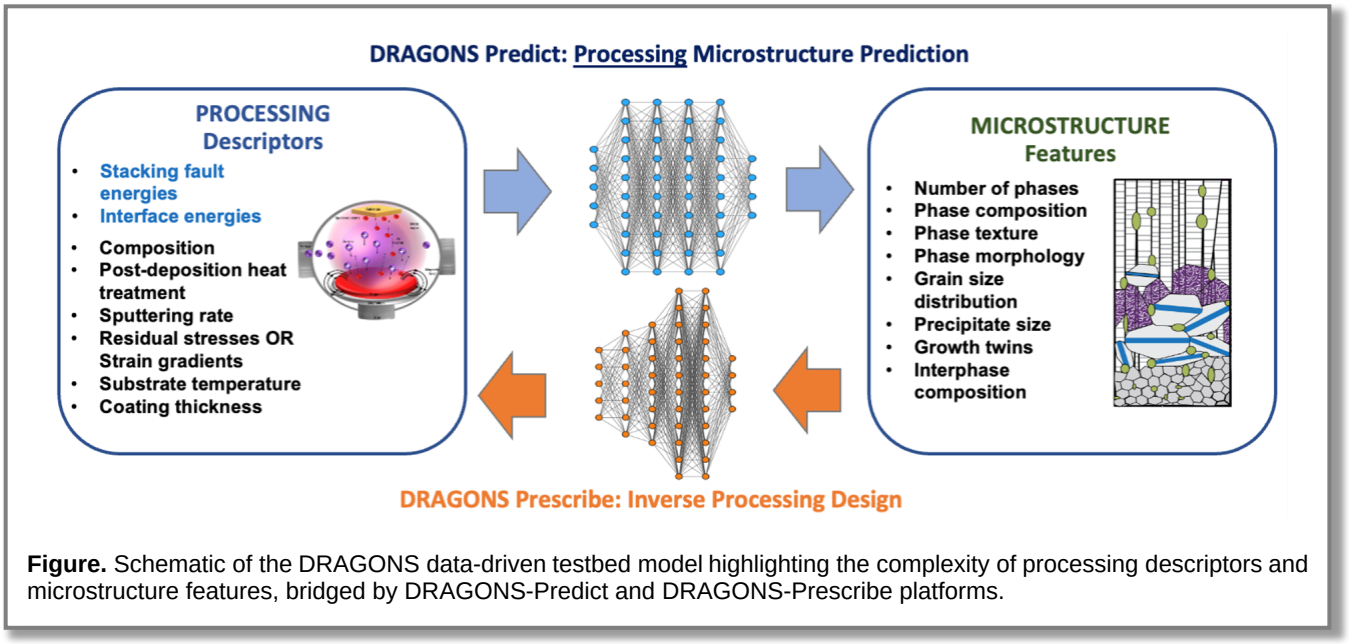


Figure. Schematic of the DRAGONS data-driven testbed model highlighting the complexity of processing descriptors and microstructure features, bridged by DRAGONS-Predict and DRAGONS-Prescribe platforms.

Relevance to MGI

The 2021 MGI strategic plan emphasizes the integration of experiment, computation, and theory through a closed, iterative feedback loop. This DMREF project achieves this by employing the DRAGONS platform to decipher processing-microstructure relationships in Ni-based superalloys. The project seamlessly integrates synthesis, characterization, and modeling tasks. Synthesis involves magnetron sputtering and heat treatment to produce complex microstructures. Characterization includes advanced diffraction and electron microscopy techniques to validate microstructural attributes. Atomistic simulations and mesoscale modeling provide predictive insights, guiding synthesis adjustments. Each cycle of synthesis, characterization, and modeling refines DRAGONS, enhancing its predictive accuracy and efficiency. This iterative approach accelerates materials discovery and development by building a comprehensive knowledge base, enabling the design of materials with specific properties. The collaborative framework ensures that experimental data inform computational models, which in turn guide further experiments, creating a synergistic loop. This integration leads to significant advances

in the understanding and manipulation of processing-microstructure relationships, thereby aligning with MGI's objectives. The project aims to expedite the discovery of processing-microstructure connections, enhancing the ability to design materials with desired functions. By generating detailed datasets and utilizing DRAGONS, this research provides a robust pathway for developing novel materials, thus significantly advancing MGI's mission.

Technical Progress

Although the project is still in its initial stage, we have made significant progress on several fronts. We decided to start building the database for Ni-based superalloys, beginning with Ni-Fe-Cr alloys. PI Hodge's team has successfully produced initial samples of binary and ternary alloys using high-throughput sputtering and PI Rupert's team is characterizing their microstructures, particularly focusing on the formation of growth twins, which are ubiquitous in Ni-based superalloys. PI Branicio's team has evaluated the stacking fault energy in binary and ternary Ni-Fe-Cr alloys using available embedded atom models (EAM) potentials and is currently assessing the formation of growth twins in thin films by performing molecular dynamics simulations of physical vapor deposition. PI Beyerlein's team has developed a phase-field model to investigate the evolution of twin structures and is currently collaborating with PI Branicio's team to fine-tune the model based on atomistic data on twin boundaries and stacking fault energies.

Future Plans

Building on our initial progress on Ni-Fe-Cr alloys, we will advance the DRAGONS platform through a multi-cycle approach to deepen our understanding of processing-microstructure relationships in Ni-based superalloys. Cycle 1 will focus on essential microstructural features like the number of phases, phase composition, and twin formation using DRAGONS-Predict and DRAGONS-Prescribe, with validation through high-throughput sputtering of Ni-Fe-Cr alloys. In Cycle 2, we will expand the feature set to include phase fraction, grain size distribution, and precipitate sizes. Cycle 3 will incorporate higher-order features such as phase morphology and boundary composition. The accuracy and generalization of DRAGONS will be evaluated in each iteration, and if necessary, the training datasets will be complemented and augmented through computational methods to improve the overall performance of the ML framework. Collaborative interactions with NIST scientists at the Material Measurement Laboratory will ensure that NIST expertise in the "integration, curation, and provisioning of critically evaluated data and models," is implemented as part of this project in regard to the MGI goals for accelerated materials development. Educational programs will include new courses and workshops on machine learning in materials science, and we will continue training undergraduate and graduate students.

Broader Impacts and Workforce Development

Since the start of this project in 2023 a new Master of Science in Materials Engineering – Machine Learning has been launched at USC. Two graduate students are being trained in magnetron sputtering and sample characterization, and two more in atomistic simulations and machine learning at USC.

Data Management and Open Access

To ensure open access to the digital data products generated by this project, data and metadata files associated with the results will be available in a GitHub repository created specifically for this project (https://github.com/tim-rupert/DRAGONS), and each data set will be assigned a digital object identifier (DOI). The repository will host both numerical and experimental data for easy accessibility by other researchers and for future use by the PIs.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The aim of the DRAGONS platform is to accelerate materials discovery and development by leveraging machine learning to rapidly establish processing-microstructure relationships, significantly reducing the time and cost compared to traditional methods. Our vision includes the creation of open-source software and databases accessible to the scientific community, promoting broader adoption and integration into various technologies. Key hurdles include ensuring data quality and model generalization across different material systems, which will be addressed through rigorous validation and collaboration with NIST scientists.

Publications and References

No publications have been submitted at this early stage, but the lead PI has presented an invited talk at the 2024 Structural Nanomaterials Conference GRC acknowledging this DMREF grant.

Designing Coherence and Entanglement in Perovskite Quantum Dot Assemblies

Lead Investigator: Libai Huang, libai-huang@purdue.edu
Participating Institutions: Purdue University, Massachusetts Institute of Technology, University of Southern California
Source of Support: NSF-DMREF
Website: none
Keywords: Exciton delocalization, Superradiance, Quantum transport, Entangled states, Light-matter interactions

Project Scope

This DMREF project aims to design a new quantum materials platform by harnessing the collective properties from coherent and entangled interactions between colloidal lead halide perovskite quantum dots (QDs). The research will build a foundation to control exciton dynamics at the individual QD level and design interactions between QDs for long-range collective coherence and entanglement. Specifically, the team will create, characterize, and model the quantum states from collective coupling between QDs and their coupling to photons in nanophotonic devices. The interdisciplinary nature of the project will also serve as an educational and outreach platform for nanotechnology and quantum science.

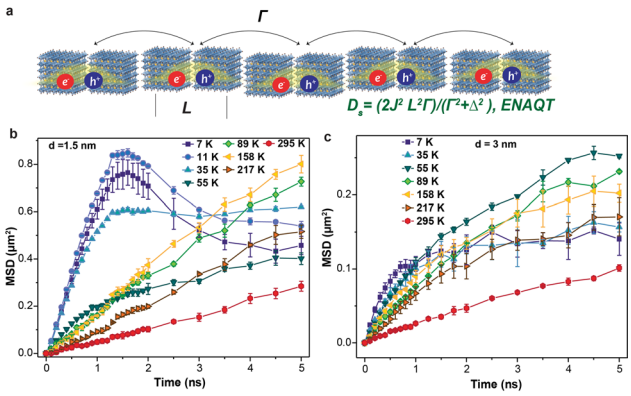


Figure. Exciton transport in a superlattice of $CsPbBr_3$ quantum dots. (a) illustration of a maximum of transport is expected when dephasing Γ is balance by energetic disorder Δ. (b-c) Exciton mean square displacement (MSD) measured for two superlattices with ligand length of 1.5 nm (b) and 3 nm (c), respectively. We observed a maximum for the steady-state diffusion at temperatures where static disorder and thermal fluctuations balance each other (158 K in b, and 55 K in c), providing evidence of ENAQT.

Relevance to MGI

This project integrates experiment, computation, and theory using a closed, iterative feedback loop among project tasks. The synthesis of perovskite quantum QDs and superlattices is guided by atomistic predictions to control exciton coupling and dephasing. These synthesized materials are then characterized using cutting-edge ultrafast microscopy and quantum optics techniques to provide real-time feedback on their properties. This characterization data informs multi-scale theoretical models, which predict and design robust quantum transport and coherence in superlattices. Finally, the project aims to manipulate multi-QD coherence and entanglement in optical cavities. The project leads to advances in quantum materials based on colloidal QDs by exploring the vast design space of perovskite structures and photonic structures. Additionally, the development of ultrafast quantum optics and quantum dynamics tools addresses key questions related to coherent interactions and entanglement in complex solid-state materials.

Technical Progress

Quantum exciton transport in superlattices. The team has demonstrated unambiguous signatures of quantum transport in $CsPbBr_3$ nanocrystal superlattices by directly imaging exciton propagation with high spatial and temporal resolutions over a temperature range of 7-298 K. At 7 K, coherent propagation of excitons dominates, with transient ballistic motion extending up to 40 NC sites. The wave-like motion interference leads to Anderson Localization in the long-time limit. As temperature increases, a peak in the long-time diffusion constant is observed at a temperature where static disorder and dephasing are balanced, providing direct evidence for environment-assisted quantum transport (ENAQT). Inspired by the transport measurements, the team explores the wave-packet motion on quantum lattices subject to stochastic noise. The analysis reveals the crucial role of spatial coherence and

predicts novel phenomena: (1) noise can enhance the transient diffusivity of spatially extended initial states; (2) the transient diffusivity has a universal dependence on initial width; (3) standing or traveling initial states, with large momentum, spread faster than a localized initial state and exhibit a noise-induced peak in the transient diffusivity. These predictions suggest the possibility of controlling the wave packet dynamics by spatial manipulations and thus extend quantum coherent control from the temporal domain to the spatial domain.

Growth and structural characterization of superlattices with different dimensionality and packing. The team has demonstrated the ability to synthesize highly ordered $CsPbBr_3$ quantum dot (QD) superlattices with a narrow size distribution and tunable inter-QD distances using long-chain organic ligands. To examine the structural ordering and packing, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected. Additionally, the team has developed a method to characterize superlattice structural disorder using STEM imaging and FFT analysis.

Exciton dephasing in single QD and dimers: Ab initio calculations have shown that $CsPbBr_3$ QD dimers exhibit 50% longer quantum coherence than monomers, because excitons become delocalized between QDs. In monomer, exciton couples strongly to the $CsPbBr_3$ highest frequency optical phonon at $130cm^{-1}$ and also to Pb-Br-Pb bending at $80cm^{-1}$. The $130cm^{-1}$ signal is significantly reduced in the dimer, due to exciton delocalization, and the $80cm^{-1}$ signal is red-shifted due to interdot coupling. Very low frequency signal due to relative QD-QD motions appear as well. Calculations have also shown that judicious choice of ligands, including π-conjugated fragments, can enhance electronic coupling between QDs, providing practical recommendations for synthesis.

Future Plans

This project was funded less than a year ago. For the remaining project periods, temperature-dependent single-particle spectroscopy and photon correlation measurements will be conducted to measure exciton linewidth, radiative lifetime, and coherent dynamics, confirming and refining theoretical predictions. Guided by theory, synthesis strategies will be developed to enhance coupling and minimize dephasing. Parameters obtained from single particle measurements will inform the model of exciton transport using stochastic wavefunction propagation in large macroscopic superlattices. The team will also manipulate both the radiative and dephasing processes in QD assemblies using optical cavities and photonic crystals, enabling robust coherence and entanglement over much longer length scales.

Broader Impacts and Workforce Development

We will train a diverse next-generation of scientists and engineers through a multidisciplinary, integrated experimental and computational approach for materials innovation, emphasizing course development and hands-on STEM outreach. (1) *Graduate and Undergraduate Student Education and Recruiting*: To encourage diverse student participation, we will leverage institutional diversity initiatives such as the Purdue Graduate Diversity Visitation Program, USC JumpStart Program, and MIT GradCatalyst Program. Additionally, we will actively recruit military veteran students through the Purdue Veterans Success Center and the Warrior-Scholar Project at USC and MIT. (2) *Physical Chemistry Lab Module*: We will develop Physical Chemistry lab module on colloidal QDs to illustrate the principle of particles confined in a 3D sphere, using absorption and PL spectroscopy to determine exciton energy. (3) *Building Apps on nanoHUB*: We will develop a summer undergraduate student program to build apps for deployment on nanoHUB.

Data Management and Open Access

nanoHUB supports the storage, security, and operational management of all data and software collected and produced by researchers of this research project. The team leverages nanoHUB for the dissemination of educational materials to a larger community.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The DMREF project accelerates materials discovery by integrating synthesis, characterization, and theoretical modeling in a closed feedback loop, reducing development time and cost. The project aims to make significant advances in quantum materials, with potential applications in quantum computing and photonics, ultimately contributing to the MGI objective of faster, cost-effective material development.

Publications and References

1. Christian M. Lange, Emma Daggett, Valentin Walther, Libai Huang, and Jonathan D. Hood. *Superradiant and subradiant states in lifetime-limited organic molecules through laser-induced tuning*. Nat. Phys. **20**, 836–842 (2024). DOI: 10.1038/s41567-024-02404-4
2. Artem V Toropin, Libai Huang, Vladimir R Nikitenko, Oleg V Prezhdo*, Extremely Non-Equilibrium Hopping Transport and Photogeneration Efficiency in Organic Semiconductors: An Analytic Approach*, J. Phys. Chem. Lett. **15**, 3884–3892 (2024). DOI: 10.1021/acs.jpclett.4c00662
3. Anna Yu Saunina, Libai Huang, Vladimir R Nikitenko, Oleg V Prezhdo, *On Analytical Modeling of Hopping Transport of Charge Carriers and Excitations in Materials with Correlated Disorder*, J. Phys. Chem. Lett. **15**, 2601–2605 (2024). DOI: 10.1021/acs.jpclett.4c00097
4. Ilia Tutunnikov, Chern Chuang, Jianshu Cao, *Coherent spatial control of wave packet dynamics on quantum lattices*, J. Phys. Chem. Lett. **14** 11632-1163 (2023). DOI: 10.1021/acs.jpclett.3c03047

DMREF: Data-Driven Integration of Experiments and Multi-Scale Modeling for Accelerated Development of Aluminum Alloys

Lead Investigator: Todd Hufnagel, hufnagel@jhu.edu
Participating Institutions: Johns Hopkins University
Source of Support: NSF-DMREF 1921959 (ensuing collaborations with DMREF 2119040, MIP 2039380, and Data CI Pilot 2129051)
Website: https://github.com/openmsi https://openmsistream.readthedocs.io/, https://openmsi.org
Keywords: data streaming, autonomy, openmsi, knowledge graph, event driven

Project Scope

The project has developed a new architectural concept to handle materials data as streams rather than discrete files to accelerate big data and complex workflows including experiments, compute, data analysis, and FAIR data curation. We've also advanced a processing-centric, knowledge-graph approach to semantic integration of materials data and workflows. The project has created OpenMSIStream, a broadly applicable, open-source software package to provide seamless connection of scientific data stores with streaming infrastructure to democratize access to the power of decoupled, real-time data streaming. Success has been measured in acceleration of project data workflows and use of OpenMSI outputs in unrelated projects.

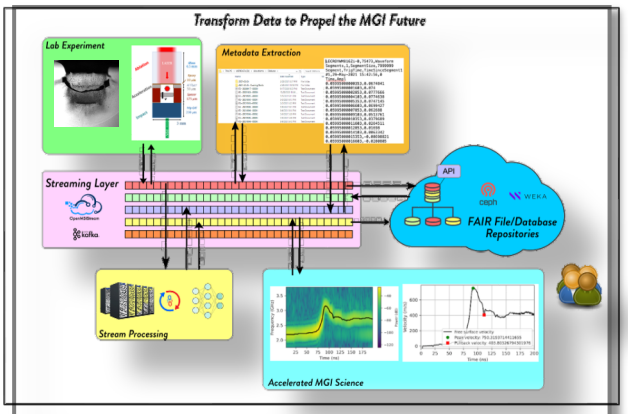


Figure. OpenMSI architecture overview highlighting decoupling of laser shock lab experiment with high-speed imaging and PDV interferometry data from automated metadata extraction, data storage, and automated, and real-time velocimetry data processing. Of note is that the data production, consumption, and processing is all automated and without human triggering of workflows. Note also that the same data is used by multiple, automated workflows simultaneously and not through serial or batch processing.

Relevance to MGI

OpenMSI creates integrated research workflows to expand MGI concepts by reversing the typical data integration paradigm built on RESTful APIs that are inherently stateless and built around polling for data. In contrast, the event-driven OpenMSI paradigm provides stateful and asynchronously linked research data, decisions, and automation information that underlies real materials research. OpenMSI creates a seamless, continuous link between stream-processing analysis and workflows with the continual, conceptual flow of research events from distributed components to close the MGI materials-by-design loop. In the OpenMSI DMREF we instantiate the platform across high-throughput X-ray and laser shock experimental laboratories, FEM modeling compute, and data curation. The project streaming brokers run on a scalable Kubernetes cluster with automated metadata extraction and data curation in Petabyte-scale CEPH object storage. The streaming backbone connects laboratory instruments, robots, and ML as well as high-performance stream processing compute resources. This is the first streaming, event-driven system for materials research designed for PI and collaborative research. OpenMSI is now in use in other projects including DMREF 2119040 (MAAP); the PARADIM MIP at Cornell and Johns Hopkins; MaterialsDigital (BAM, Berlin); two DEVCOM HTMDEC high-throughput Centers; the IMQCAM NASA STRI Digital Twin in metal additive manufacturing; and the NSF VariMat Cyberinfrastructure Pilot linking PARADIM and Quantum Foundry data.

Technical Progress

OpenMSI released and updated the OpenMSIStream package[1] and continues to add functionality including data consumers for S3 storage and the Girder data framework. We delivered a short course to over 30 new users with open release of course materials (https://github.com/openmsi/openmsistream_short_course). Our project streaming broker cluster, based on Apache Kafka, was moved from the commercial Confluent Cloud to an on-prem, Kubernetes cluster providing significant reduction in cost and higher performance through high-speed networking. Our on-prem brokers provide dynamic scaling and allow us to provide free prototyping for interested, outside projects to trial OpenMSI in their own laboratories. We have migrated stream processing from ksqlDB to Apache Flink. Automated metadata extraction has been shared internationally at a MADICES hackathon and is moving to incorporate the PARADIM Project Chameleon file format interoperability API. Two papers highlighting instantiation of OpenMSI research for inverse design of alloys have been published[2,3].

Future Plans

OpenMSIStream is now a mature product that will be enhanced through addition of broadly applicable data-consumers as needed, bug corrections, and performance enhancement. The success of the OpenMSIStream Short Course provides a basis to deliver similar content to a broader audience and release a short series of tutorial videos to encourage adoption. We will support the growing base of adopters through direct assistance and GitHub pull requests. OpenMSIStream Documentation[4] is mature but will include updates as features are added and new tutorial examples are created. OpenMSI capture of metadata from spall nucleation modeling will be developed and a stream processing system to automate the modeling workflows will be completed by the end of the project. The OpenMSIModel knowledge graph modeling package will move from beta to version 1.0 in the fall. A short course on knowledge graph modeling using OpenMSIModel will be planned.

Broader Impacts and Workforce Development

OpenMSI supported training of three graduate students, six undergraduates, and two research data engineers. The OpenMSIStream Short Course delivered hands-on experience with data streaming and project software to over 30 students from multiple universities and the Army Research Laboratory. Development of an event-based approach to MGI science has already created new paradigm being used in NSF, NASA, DEVCOM, and international projects spanning diverse universities and facilities. OpenMSI has supported work of under-represented groups including women, students of color, and a student from an HBCU. An important legacy of the project will be the broader impact on how MGI work conceptualizes data-linked workflows as a foundation for autonomous research.

Data Management and Open Access

OpenMSI provides primary support for FAIR data by providing automated metadata extraction and data curation. This significant community advance moves much of the burden of curation from investigator to infrastructure. By moving data curation to the front of the workflow pipeline, OpenMSI create a path for curation and release of dark data as part of routine data workflows. OpenMSI code development and products are documented and released under open license in 14 public repositories[5]. OpenMSI has embraced release of data in a modified version of the NSF DIBB WholeTale data curation platform and extended that platform in a number of collaborating projects (notable DEVCOM HTMDEC, NSF PARADIM, and NASA IMQCAM). A FAIR data compliant dataset for OpenMSI-project-specific publications is available with DOI[6].

Advancing Along the Materials Development Continuum and Partnerships to Translation

OpenMSI provides a conceptual framework and open source tools to realize a new paradigm for MGI materials science. The decoupled nature of the framework allows research distributed in time and space to democratize access to the research enterprise. The knowledge graph approach to data semantics provides a powerful framework to enable data reuse from the earliest stages of materials discovery through technical readiness levels and product delivery. These concepts are being pursued in collaborating projects and form the basis for autonomous research which will translate rapidly to product manufacturing spaces. Follow-up funding will focus on advancing the tools to integrate these ideas with Materials Acceleration Platforms (MAPs) for autonomous laboratories.

Publications and References

1. Eminizer et al., (2023). OpenMSIStream: A Python package for facilitating integration of streaming data in diverse laboratory environments. Journal of Open Source Software, 8(83), 4896, https://doi.org/10.21105/joss.04896

2. Wu, Dung-Yi and Miao, Chengyun and DiMarco, Christopher S. and Ramesh, K.T. and Hufnagel, Todd C. Microstructural effects on the spall failure of 7085 aluminum alloy. *Materials Science and Engineering: A* , v.866 , 2023 https://doi.org/10.1016/j.msea.2023.144674 Citation Details

3. Wu, Dung-Yi and Hufnagel, Todd C. Efficient searching of processing parameter space to enable inverse microstructural design of materials. *Acta Materialia* , v.264 , 2024 https://doi.org/10.1016/j.actamat.2023.119562 Citation Details

4. https://openmsistream.readthedocs.io/

5. https://github.com/openmsi

6. FAIR Dataset: https://doi.org/10.34863/vr58-pd46.

Compatibilized polymer blends

Lead Investigator: Robert Joseph Spence Ivancic, robert.ivancic@nist.gov
Participating Institutions: NIST
Source of Support: NIST
Website: none
Keywords: polymer blends, block-copolymers, mechanics, crystallization, molecular dynamic simulations

Project Scope

Polymer blends see extensive use from packaging and automobiles to tissue scaffolding and gas separation. While these blends are ubiquitous, their typically brittle behavior limits their application. This project aims to design compatibilizers to toughen these blends. Here, we use molecular dynamics simulations to study how these materials order at the interface and how their interfacial structure affects mechanical properties. We will test and create theories of compatibilization, reducing the cost and increasing the mechanical stability of compatibilized blends.

Relevance to MGI

Simulations and experiments provide complimentary ways to examine theories of polymer compatibilization. Molecular dynamics simulations provide access to compatibilizer configurational details that are not typically available in experiments. Experiments provide access to length and timescales that are not within reach of molecular dynamics simulations. As such, we ensure our theories align with existing experimental data. Moreover, we are collaborating with an experimental colleague (Dr. Aaron Burkey) who have synthesized deuterated compatibilizers. We plan to use these materials to understand how compatibilizers affect crystallization at polymer interfaces.

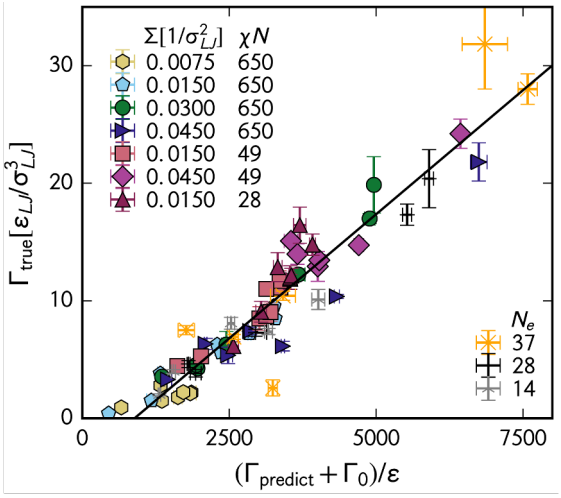


Figure. True toughness as measured by molecular dynamics simulations against scaled predicted toughness from our theory of compatibilized amorphous polymer blends. Simulations cover a wide range of compatibilizer areal densities (Σ), Flory-Huggins parameters (χN), and entanglement lengths (N_e).

Technical Progress

We recently published our novel theory of how compatibilizers toughen amorphous polymer interfaces. This work uses molecular dynamics simulations to provide evidence for a microscopic, physics-based theory of the toughness of compatibilized glassy polymer blends. It then uses self-consistent field theory to parameterize the microscopic parameters in this model to make the model useful to our industrial partners. Finally, it tests this model on both simulated and experimental data.

Our project is now considering how crystallization affects this work. This is important as semicrystalline polymers make up more than two-thirds of commodity plastics produced today. We have performed molecular dynamics simulations of a polymer blends with diblock block-copolymer compatibilizers using a coarse-grained model of a polymer that crystallizes in a realistic way. We have found increasing diblock length increases the size of the amorphous region near the interface. Moreover, high diblock areal density increases the amount of compatibilizer-compatibilizer crystallization near the interface. These observations will yield better theoretical models of semicrystalline polymer blend compatibilization.

Future Plans

In the future, this project will be split into two directions. First, we plan to continue our efforts to develop a comprehensive theory to describe the toughness of compatibilized semicrystalline polymer interfaces which are key to industry. Here, we will use molecular dynamics simulations combined with experiments done by our colleagues to test potential theoretical frameworks. Second, we plan to use the theory we developed for amorphous polymer blends and use generative machine learning to solve the inverse design problem, *i.e.*, given two polymers and a budget of compatibilizer monomers, what is the optimal compatibilizer?

Broader Impacts and Workforce Development

This project contributes to workforce development by equipping students with advanced skills in molecular modeling, computational chemistry, and materials science. It has done this by taking on summer undergraduate students and training them to code, to perform molecular dynamics simulations, and to think using physical principles. Moreover, the project encourages interdisciplinary collaboration, enabling participants to work effectively across various scientific domains and promoting an integrated understanding of complex material systems.

Data Management and Open Access

A key objective in this project is to produce FAIR data that can be used to spur advances by future researchers. The data and code to reproduce our most recent work the DOI is available at: *doi:10.18434/mds2-3057*.

Advancing Along the Materials Development Continuum and Partnerships to Translation

This project leverages the MGI framework to accelerate the development and optimization of novel compatibilizers for polymer blends. The combination of using experiments and simulations to test theory drastically reduces compatibilizer development time as compared to traditional trial-and-error methods. The theories that are developed in this project will be integrated into industry to allow for smarter, faster compatibilizer design.

Publications and References

1. R. J. S. Ivancic and D. J. Audus, *Predicting compatibilized polymer blend toughness*, Science Advances **10**, (2024). doi:10.1126/sciadv.adk6165

FLOSIC: Efficient Density Functional Calculations without Self-interaction

Lead Investigator: Koblar A Jackson
Participating Institutions: Central Michigan University, University of Texas at El Paso, Tulane University, University of Pittsburgh, University of Florida at Gainesville
Source of Support: DOE-BES
Website: https://www.flosic.org
Keywords: Self-Interaction Correction, Improved Density Functional Theory, Magnetic Molecules, Design Rare-Earth Systems, Computing for Energy Efficiency

Project Scope

The FLOSIC Center is one of the Computational Chemical Sciences Centers funded by the U.S. Department of Energy. The goal of the Center is to produce open-source software for efficient computational modeling of materials for energy and information technologies, within a density-functional framework that is free of the unphysical effects of electron self-interaction, the major flaw present in existing density functional theory (DFT) methods. This entails improved and more efficient computational algorithms and improved density functional approximations. Target applications are to more accurately describe charge-transfer excitations in vacuum and solution and quantitative descriptions of f-electron devices.

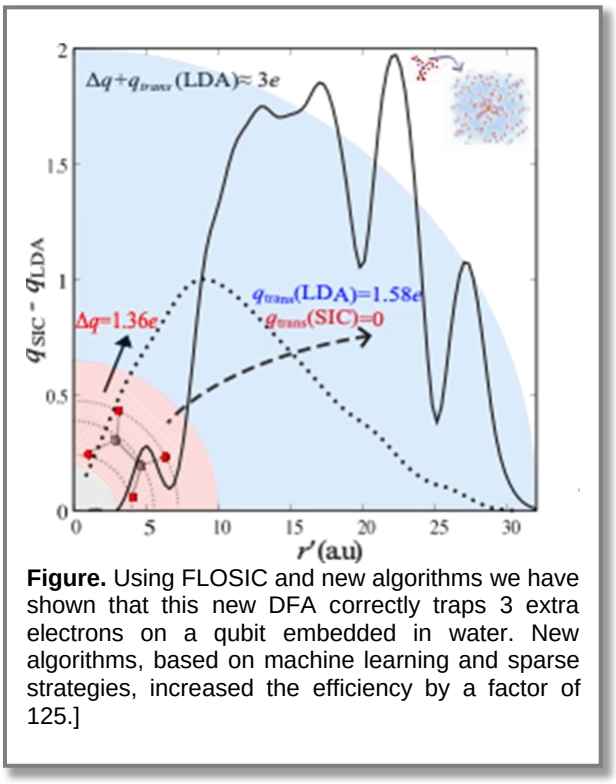


Figure. Using FLOSIC and new algorithms we have shown that this new DFA correctly traps 3 extra electrons on a qubit embedded in water. New algorithms, based on machine learning and sparse strategies, increased the efficiency by a factor of 125.]

Relevance to MGI

Project integrates computation, experiment, and theory and iteratively improves both computation and theory through feedback between sub-projects. Huge databases of energies as a function of the Fermi-Orbital Descriptors give opportunities to data-analysis and machine learning based advances. The Tulane group leads new theoretical approximations to DFT. Computational implementation and testing on small molecules are performed by UTEP and CMU. CMU and Pitt scale-up these molecules to develop models of systems that can be synthesized and characterized by the University of Florida. Since 2021, the UTEP group shifted its emphasis from legacy parallelization and ease of use to new algorithms for f-electron systems and charged hydrated complexes through new massively parallel sparse workflows. This reduces time to solution. Demonstrations of theory-to-computation feedback identified during the first phase of this project revealed that for gapped systems the FLOSIC theory was constrained to deliver real orbitals. This presented a conundrum since it is well known that inclusion of the spin-orbit interaction creates complex Kohn-Sham orbitals that would seemingly create prospects for enhanced energy lowering of the FLOSIC orbitals. As a result, a generalization to include complex Fermi-Orbital Descriptors improved descriptions of magnetic systems with unquenched orbital moments such as in rare-earth applications.

Technical Progress

Real Fermi–Löwdin orbitals (FLOs) were introduced to recast the self-interaction correction into an explicitly unitarily invariant form. The FLOs are generated from a set of *N* quasi-classical electron positions, referred to as

Fermi-Orbital descriptors (FODs), and a set of *N*-orthonormal single-electron orbitals. FOD positions, when optimized, minimize the total energy. More recently, we introduced complex Fermi orbital descriptors (FODs) in the FLOSIC method. With complex FODs, the Fermi–Löwdin orbitals (FLOs) used to evaluate the SIC correction to the total energy become complex. Complex FLO-SIC (cFLOSIC) calculations based on the local spin density approximation produce total energies that are generally lower than the corresponding energies found with FLOSIC restricted to real orbitals (rFLOSIC). The energy lowering stems from the exchange–correlation part of the self-interaction correction. The Hartree part of the correction is more negative in rFLOSIC. The energy difference between real and complex solutions is greater for more strongly hybridized FLOs in atoms and for FLOs corresponding to double and triple bonds in molecules. The case of N_2 was examined in detail to show the differences between the real and complex FLOs. We show that the complex triple-bond orbitals are simple and physically appealing combinations of π and σ_g orbitals that have not been discussed before. Consideration of complex FODs, and resulting unitary transformations, underscores the fact that FLO centroids are not necessarily good guesses for FOD positions in a FLOSIC calculation.

Creating initial sets of starting FODs that lead to a positive definite Fermi orbital overlap matrix proved to be a challenge for heavier atoms. We developed a proof that guarantees the existence of a FLOSIC solution and further guarantees that if a solution for N electrons is found, it can be used to generate a minimum of $N-1$ and a maximum of $2N-2$ initial starting points for systems with fewer electrons. To extend to applications for rare-earth systems, the new algorithm computationally mined quantum information from element 118 and demonstrated automated construction of initial Fermi–Löwdin-Orbital (FLO) starting points for all elements in the Periodic Table. It will enable a means for constructing a small library of scalable FLOs for universal use in molecular and solid-state calculations and can be systematically improved for greater efficiency and for applications to excited states such as x-ray excitations and optically silent excitations. Applications to heavy and super-heavy atoms are presented. All starting solutions reported here were obtained from a solution for element 118, Oganesson.

We developed a data-intensive method that can be used to carry out self-consistent Fermi–Löwdin–Orbital-Self-Interaction corrected calculations (FLOSIC) on a *trianion* in solution. The calculations give a physically correct description of the electronic structure of the *trianion* and water. In contrast, uncorrected local density approximation (LDA) calculations result in approximately half of the anion charge being transferred to the water bath due to self-interaction error (see figure). Use of group-theory and the intrinsic sparsity of the theory decreased computer time by a factor of 125. Comparisons between low-rung quantum-chemical methods and FLOSIC were provided.

Future Plans

We plan to continue to increase the efficiency, with respect to computer time and electrical power usage, of the code until we make FLOSIC calculations, on a per-geometry basis, more efficient than DFT calculations. That such a goal can be achieved is expected due to the fact that the localization of the FLOSIC orbitals is greater than that of the equivalent DFT orbitals.

Broader Impacts and Workforce Development

Over 30 graduate students have been a part of this project. They have gone on to work as postdoctoral associates, and program directors at computing companies. Students are given chances to take follow-on specialized graduate-level courses that are designed to more quickly export these capabilities to cloud computing.

Data Management and Open Access

The FLOSIC method is publically available at the website above. All papers are are also available there.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The method allows for design of materials for catalysis, batteries, photovoltaics, and quantum sensors and computing components by ensuring that charge transfer and shell structures are correct. The FLOSIC2023 implementation is being adopted with follow-on-funding by a PNNL-led project that goes beyond github-based distributions of the codes and allows for cloud-based quantum learning, quantum computing and quantum design. Special courses, involving CMU, UTEP and PNNL are preparing the next generation workforce.

Publications and References

1. R. Maniar, K.P.K Withanage, C. Shahi, A.D. Kaplan, J.P. Perdew and M.R. Pederson, *Symmetry breaking and self-interaction correction in the chromium atom and dimer*, Chem. Phys. **160** 144301 (2024). https://doi.org/10.1063/5.0180863
2. D.B. Nguyen, K.A. Jackson and J.E. Peralta , *Bond length alternation of pi-conjugated polymers predicted by the Fermi-Lowdin orbital self-interaction correction method,* J Chem. Physic. **160** 014101 (2024), https://doi.org/10.1063/5.0178251 (2024).
3. J. I. Melo, M. R. Pederson, and J. E. Peralta, *Density Matrix Implementation of the Fermi-Lowdin Orbital Self-interaction Correction Method*, J. Phys. Chem. A, **127**, 527 (2023). DOI: https://doi.org/10.1021/acs.jpca.2c07646.
4. S,Ruan, K,A. Jackson, and A. Ruzsinszky, *Spin-crossover complexes: Self-interaction correction vs. density correction*, J. Chem. Phys. **158**, 064303 (2023) https://doi.org/10.1063/5.0128950.
5. M. R. Pederson, A. I. Johnson, K. P. K. Withanage, S. Dolma, G. B. Flores, A. Hooshmand, K. Khandal, P.O. Lasode, T. Baruah, and K. A. Jackson. *Downward Quantum Learning from Element 118: Automated Generation of Fermi-Löwdin Orbitals for all Atoms*, J. Chem. Phys. 158, 084101 (2023). DOI: https://doi.org/10.1063/5.0135089.
6. P. Shukla, P. Mishra, T. Baruah, R. R. Zope, K.A. Jackson, and J.K. Johnson, *How do self-interaction errors associated with stretched bonds affect barrier height predictions?* J. Phys. Chem. A 2023, 127, 7, 1750–1759 (2023) https://doi.org/10.1021/acs.jpca.2c07894.
7. A. R. Hale, M. E. Lott, J.E. Peralta, D. Foguet-Albiol, K.A. Abboud, G. Christou, *Magnetic properties of high nuclearity Fe_x-oxo (x = 7, 22, 24) clusters analyzed by a multi-pronged experimental, computational, and magnetostructural correlation approach*, Inorganic Chemistry **61**, 11261 (2022) https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c01371.
8. K.P.K. Withanage, K.A. Jackson, and M.R. Pederson, *Complex Fermi-Löwdin Orbital Self-interaction correction*, J. Chem. Phys. **156**, 231103 (2022) https://doi.org/10.1063/5.0091212
9. K.P.K. Withanage, K. Sharkas, J.E. Peralta, J.K. Johnson, J. P. Perdew and K.A. Jackson, *Fermi-Löwdin Orbital Self-interaction correction of adsorption energies on transition metal ions*, J. Chem. Phys. **156**, 134102 (2022). DOI: https://doi.org/10.1063/5.0078970.
10. P. Mishra, Y. Yamamoto, J.K Johnson, K.A. Jackson, R.R. Zope, and T. Baruah, *Study of self-interaction-errors in barrier heights using locally scaled and Perdew-Zunger self-interaction methods*, J. Chem. Phys. **156**, 014306 (2022) https://doi.org/10.1063/5.0070893.
11. A.R. Hale, L.E. Aebersold, J.E. Peralta, D. Foguet-Albiol, K. A. Abboud and G. Christou, *Analysis of spin frustration in an Fe^{III}_7 cluster using a combination of computational, experimental, and magnetostructural correlation methods*, Polyhedron **225**, 116045 (2022) https://doi.org/10.1016/j.poly.2022.116045.
12. C.M. Diaz, L. Basurto, S. Adhikari, Y. Yamamoto, A. Ruzsinszky, T. Baruah, and R.R. Zope, *Self-interaction-corrected Kohn-Sham effective potentials using the density-consistent effective potential method,* J. Chem. Phys. **155**, 064109 (2021) https://doi.org/10.1063/5.0056561.
13. D.B. Nguyen, M.R. Pederson, J.P. Perdew, K.A. Jackson, and J.E. Peralta, *Initial Fermi orbital descriptors for FLOSIC calculations: The quick FOD method,* Chem. Phys. Lett. **780**, 138952 (2021); DOI: https://doi.org/10.1016/j.cplett.2021.138952.
14. S. Akter, J.A. Vargas, K. Sharkas, J.E. Peralta, T. Baruah, K.A. Jackson, and R. R. Zope, *How well do self-interaction corrections repair the over-estimation of static polarizabilities in density functional calculations?*, Physical Chemistry Chemical Physics **23**, 18678 (2021); DOI: https://doi.org/10.1039/d0cp06512a.
15. K. Wagle, B. Santra, P. Bhattarai, C. Shahi, M.R. Pederson, K.A. Jackson, and J.P. Perdew, *Self-interaction Correction in Water-ion Clusters*, Journal of Chemical Physics **154**, 094302 (2021); DOI: https://doi.org/10.1063/5.0041620.
16. P. Bhattarai, B. Santra, K. Wagle, Y. Yamamoto, R.R. Zope, A. Ruzsinszky, K.A. Jackson, and J.P. Perdew, *Exploring and enhancing the accuracy of interior-scaled Perdew-Zunger self-interaction correction,*. Journal of Chemical Physics **154**, 094105 (2021); DOI: https://doi.org/10.1063/5.0041646.
17. P. Bhattarai, K. Wagle, C. Shahi, Y. Yamamoto, S. Romero, B. Santra, R. R. Zope, J. E. Peralta, K. A. Jackson, and J. P. Perdew, *A step in the Direction of Resolving the Paradox of Perdew-Zunger Self-Interaction Correction. II. Gauge Consistency of the Energy Density at Three Levels of Approximation.* Journal of Chemical Physics **152**, 214109 (2020); DOI: https://doi.org/10.1063/5.0010375.
18. K. P. K. Withanage, S. Akter, C. Shahi, R. P. Joshi, C. Diaz, Y. Yamamoto, R. Zope, T. Baruah, J. P. Perdew, J. E. Peralta, and K. A. Jackson, *Self-interaction-free electric dipole polarizabilities for atoms and their ions using the* Fermi-Löwdin self-interaction correction (FLO-SIC), Phys. Rev. A **100**, 012505 (2019). DOI: https://journals.aps.org/pra/abstract/10.1103/PhysRevA.100.012505.

19. K. Trepte, S. Schwalbe, T. Hahn, J. Kortus, D-y. Kao, Y. Yamamoto, T. Baruah, R. R. Zope, K. P. K. Withanage, J. E. Peralta, and K. A. Jackson, *Analytic Atomic Gradients in the Fermi- Löwdin obital self-interaction correction.* J. Comp. Chem. **40**, 820 (2019); https://onlinelibrary.wiley.com/doi/10.1002/jcc.25767.
20. K.P.K. Withanage, K. Trepte, J, E. Peralta, T, Baruah, *On the question of the total energy in the Fermi- Löwdin orbital self-interaction correction method*. J. Chem. Theory Comput. **14**, 4122 (2018) https://pubs.acs.org/doi/10.1021/acs.jctc.8b00344.

DNA-Nanocarbon Hybrid Materials for Perception-Based, Analyte-Agnostic Sensing

Lead Investigator: Anand Jagota (Principal Investigator), anj6@lehigh.edu
Participating Institutions: Lehigh University, Memorial Sloan Kettering Cancer Center, National Institute for Standards and Technology
Source of Support: NSF-DMREF
Website: none
Keywords: Analyte-Agnostic Trainable Molecular Perceptron, Nanosensor Array, Materials for Perception, Machine Learning

Project Scope

Sensing of specific bio-molecules is the basis of many diagnostic tools. We propose a novel approach to detecting analytes and physiological states using an artificial perception system we call an Analyte-Agnostic Trainable Molecular Perceptron (AATMP). The AATMP comprises an array of hybrid nanomaterials that can be interrogated with high-throughput spectroscopy. Training of machine learning algorithms on the nanosensor responses to various analytes or biofluids can allow for the array to recognize a variety of biomarkers and conditions. Our goal is to demonstrate the capability of this platform to act as a universal molecular sensing tool.

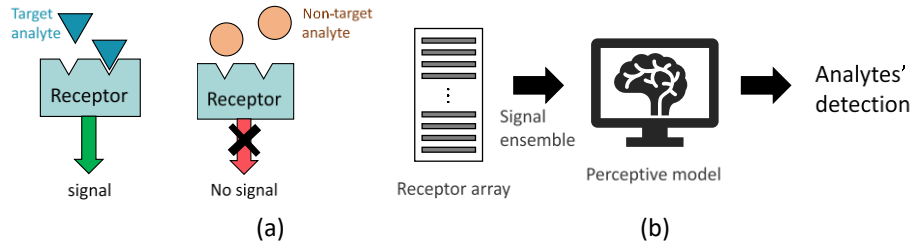


Figure 1: (a) Sensing based on one-to-one recognition. Example: Lock-and-key mechanism in which the target analyte binds specifically and selectively to its receptor as in antibodies. (b) Sensing based on perception: Multiple sensing elements provide signals. A machine learning model connects inputs to an output, e.g., analyte presence. The sensor array and trained model together form the perceptive sensing model.

Relevance to MGI

This project applies machine learning to develop universal sensing tools with broad diagnostic applications. This represents a shift from traditional lock-and-key sensor mechanisms towards novel technologies that take advantage of advancements in the field of artificial intelligence and nanotechnology. The nanosensors used in this technology are constantly being evaluated and improved upon by assessing their performance as data generators for machine learning. This work requires a multidisciplinary team of engineers, chemists, computer scientists, and materials scientists. The outcome of this work, trainable sensor arrays capable of diagnosing many diseases, has important translational medical applications as well as an ability to further our understanding of the interactions between carbon nanotubes and biomolecules. This will be informative for the broader field of materials science. The insights we gain as to nanosensor-biomolecule interactions will also guide the development of improved nanosensors for specific diagnostic applications. Overall, this work allows for critical diagnostic tool developments that will enable multidisciplinary research advancements.

Technical Progress

- **Improvement to Production of Nanosensor Array Elements:** To improve the production of our nanosensor arrays, we have developed a novel method to generate quantum well defect/organic color center-modified carbon nanotubes with diazonium salts, using hydrogen peroxide as a reducing agent. This efficient reaction occurs under significantly more mild conditions than possible with previous functionalization strategies. This new method enables functionalization with pristine, unwrapped SWCNTs, facilitating scale-up to higher yields than previously possible. The reaction can also be conducted on polymer-wrapped carbon nanotubes, including DNA-encapsulated SWCNTs, without destroying the wrapping and while preserving stability of the suspension, facilitating the rapid synthesis of larger, more-diverse arrays of nanosensors. The new method also enables the degree of nanotube functionalization to be continuously monitored via fluorescence spectroscopy, allowing for more precise control of functionalization and greater consistency between different nanosensor batches.

- **Advances in Chirality-Sensing.** Since the issuance of the award, we have expanded the use of DNA in our DNA-SWCNT hybrids to include both the naturally-occurring D-DNA and its mirror-image L-DNA. As a result, we are now able to prepare enantiomeric pairs of DNA-SWCNTs. We have shown that a pair of sensors made of such enantiomeric pairs, which we call bilateral chiral gauge or BCG, can pick up chirality information of an analyte (Figure 2). We speculate that a molecular perceptron made of an array of BCG is better suited for probing intrinsically chiral biofluids. Future work will be geared towards testing this hypothesis.

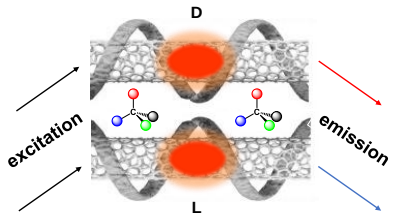


Figure 2: Enantiomeric pairs of DNA-SWCNTs provide new functionality in our nanosensors, potentially making better sensors for chiral molecules.

- **Progress in Optimization of Nanosensor Array Elements.** A central hypothesis of our program is that optimal collections of nanosensor array elements can be discovered and trained for multiple sensing tasks. Development of this materials system comprises three parts: (A) Finding an optimal set of nanosensors, starting with a library of resolving DNA-SWCNT hybrids, (B) Training and further optimization of the AATMP for a particular target task, given a nanosensor array and labeled samples for machine learning, and (C) Optimized coarse-grained (CG) and all-atom molecular modelling to understand the structural and physical basis of sensor/analyte interactions. We have made progress in tasks (A and B) with choices based on retrospective feature importance analysis and on unsupervised selection of a subset based on a mutual orthogonality score.

Future Plans

The focus of this project going forward will be on the selection of a set of DNA-SWCNT hybrids to compose the nanosensor array, development of coarse grain (CG) and all-atom molecular simulations, and demonstration of detection of different physiological states starting with the same analyte-agnostic library of nanosensor elements. We will test the efficiency of the optimized AATMP process first by assessing sensitivity to specific protein and metabolite biomarkers. This will enable improved sensing and biomarker discovery for multiple disease indications.

Broader Impacts and Workforce Development

The multidisciplinary and collaborative nature of this research program provides excellent educational and training opportunities for graduate students. Davison and Jagota will co-train the Lehigh students working in different computational modeling and machine learning areas. Heller will mentor students from a range of PhD programs within Weill Cornell Medical College and MSKCC through the new Cancer Engineering PhD Program in the Gerstner Sloan Kettering Graduate School, of which Dr. Heller serves as Co-Director. Similarly, post-doctoral associates across all three labs are encouraged to actively share cross-disciplinary knowledge. A major outreach activity we have conducted is to run SWCNT sorting camps to train researchers in the field. Ming Zheng and his NIST colleague Dr. Jeffrey Fagan initiated the three-day SWCNT training camp in August 2023. By now we have successfully held 4 sessions and trained > 20 participants from around the world.

Data Management and Open Access

At the time of publication, all data sets will be available upon request. The source data for the machine learning will be published. Codes for the machine learning and data analysis will be available upon request for research purposes.

Advancing Along the Materials Development Continuum and Partnerships to Translation

With the MGI's support, we have brought together individuals with expertise in chemistry, nanomaterials, engineering, and artificial intelligence to enable impactful, multidisciplinary research advancements. Through this collaborative project, improvements are being made in how nanosensors are designed, synthesized, and how the data obtained from them is evaluated and applied in machine learning models. We envision the AATMP platform being implemented as diagnostic tools to detect many diseases and conditions that lack specific, known biomarkers, and for early disease detection. This technology has broad commercialization applications for this purpose and to detect other analytes of interest, such as environmental toxins and drugs of abuse. Additional work to validate and further improve this technology is needed for our tools to become broadly and commercially available.

Publications and References

1. S. Piletsky, E. Keblish, and D. A. Heller, *Controlled aryl quantum well formation on biopolymer-wrapped carbon nanotubes mediated by hydrogen peroxide*, Submitted. DOI: 10.26434/chemrxiv-2024-8f3jf-v2
2. M. Kim, J. J. McCann, J. Fortner, E. Randall, C. Chen, Y. Chen, Z. Yaari, Y. Wang, R. L. Koder, D. A. Heller, *Quantum Defect Sensitization via Phase-Changing Supercharged Antibody Fragments*, J. Am. Chem. Soc. **146**, 12454-12462 (2024). DOI: 10.1021/jacs.4c00149

Rheostructurally-informed Neural Networks for geopolymer material design

Lead Investigator: Safa Jamali, s.jamali@northeastern.edu
Participating Institutions: Northeastern University, University of Delaware, Georgetown University
Source of Support: Enter NSF-DMREF
Website: none
Keywords: Geopolymers, Physics-informed machine learning, Soft matter, rheology.

Project Scope

Geopolymers are inorganic and non-crystalline structural materials that can be obtained from natural soils via a chemical activation. They have great potential as additives to reduce cement consumption in construction and thus can help reducing green-house gas emissions of cement manufacturing. They also promote the adoption of local soil resources for traditional and 3D printing-based construction. Important for human space exploration, geopolymers can be also formed from lunar and Martian soils with limited water, and thus are excellent candidates for space infrastructure such as landing pads and shelters.

Relevance to MGI

Variety of geopolymers and the intertwining of different processes at play in forming them, makes their design cycle extremely long and difficult. By combining a range of advanced computational tools with experiments, we are developing neural networks that are informed by the micro-, meso-, and macro-scale. Employing the latest advances in physics-informed AI, we are developing the next generation of predictive meta-models and enable advanced approaches for sustainable manufacturing of structures from geopolymers. Our approach to understanding the true multi-scale multi-physics nature of these systems lies in the complementary application of experiments, computation, and data-driven methods across multiple scales. While no individual PI's capabilities and expertise span over all three scales, all PIs have access to the mesoscale gel properties either through simulations, modelling or experiments, providing a reliable checkpoint for flow of information from one scale to another as well as multiple opportunities for rigorous cross-validation, bench-marking, and iterative feedback between experimental and computational approaches. We have built cross-team collaborations on different fronts: (1) experimental efforts are designed based on the simulations performed in both Jamali and Del Gado groups, (2) data-driven tools and models are developed based on the experimental results from the Wagner group, (3) constitutive models to describe mechanics of geopolymeric gels are developed by integrating experiments and simulations, into the machine learning platforms.

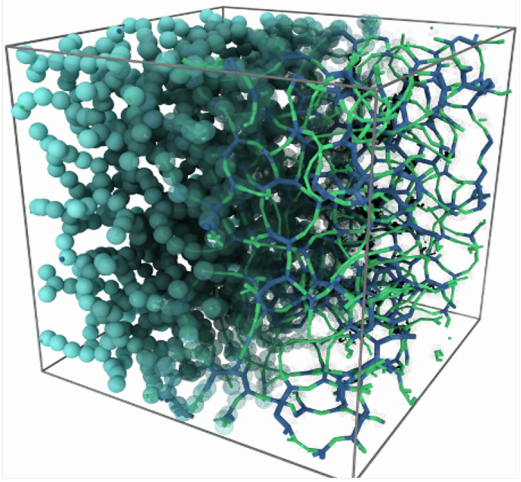


Figure. Schematic structure of a geopolymer network spanning the entire sample with complex elastoviscoplastic mechanics.

Technical Progress

In order to best present advances made, we report on the technical progress with respect to each thrust of the project:

(a) **Experimental effort:** The Wagner team at the UD has successfully applied stop-flow SAXS experimentations on the gels to better understand the kinematics and real-time mechanical evolution of different geopolymeric systems as they form. These are then paired with the rheo-kinetic measurements for a wide range of aluminosilicate gels to better undetstand the role of material composition on its final rheology/mechanics. These efforts have shown in great details how the individual particle size, particle cluster size, as well as the overall particle network fractal dimension changes during gelation.

(b) **Computational effort:** The Del Gado group at Georgetown, and the Jamali group at Northeastern have both made significant progress in terms of developing massively large-scale computational tools that can be directly used to better study and understand geopolymeric systems. Building upon previous works of both groups, Del Gado group has extensively studied the rheology of different geopolymeric systems under conditions relevant to processing, as well as during formation of a space-spanning gel. The Jamali group on the other hand has used a series of network science tools to understand the collective dynamics of these gels at the meso-scale. By doing so, the two teams have for the first time developed models that span individual (nano meter) scale simulations, to larger assemblies at the milimeter scale where mechanics of the system can be interrogated and studied without compromising essential physics.

(c) **Data-driven efforts**: The Jamali group at Northeastern has made significant progress towards building physics-informed machine learning tools: (1) developing machine learning algorithms that discover underlying constitutive relations from experimental and computational data for a specific unknown material. This is done in an unbiased manner, and has resulted in learning new physical insights for model systems such as Carbopol. (2) machine learning models have been developed fully capable of solving fractional and integer order integro-differential equations. This enables the team to study nonlocal rheological models, and build memory effects into the constitutive equations that are either used or discovered from the experimental and computational studies. (3) multi-fidelity data-driven platforms that provide extremely accurate predictions of an observed quantity (rheology, mechanics, structural characteristics, etc.) by combining high fidelity experiments as well as low fidelity model or simulation predictions. The team has established these multi-fidelity platforms to be extremely effective digital rheometers.

Future Plans

The team plans to combine efforts in the final year of the project to test, model, and design realistic geopolymeric materials as viable reactive binders with promising mechanical properties. These efforts will allow the team to identify a number of candidate material systems that can be then studied with regards to their manufacturabilities. This will involve a much deeper study of rheological features in flows that are relevant to additive and conventional manufacturing processes, as well as extending the system to mixtures of cementitious materials as well as geopolymeric systems. The size disparity in constituents of such mixtures will pose another level of complexity that may warrant follow up research.

Broader Impacts and Workforce Development

During the period of this project, 3 Postdocts, 6 PhD students, as well as several masters and undergraduate students have been trained. Two graduate students have also collaborated closely with the scientists at the Wright-Patterson Air-Force Lab personnel during their summer residency/internship programs, and a postdoctoral associate is involved with the researchers at NIST for their activities in this project. From an environmental perspective, geopolymers present a great promise for replacing at least partially cement and other carbon emitting structural materials. The methods developed under the overarching efforts in this project are directly applicable to not only other material systems, but to many disciplines far beyond its immediately intended community.

Data Management and Open Access

All codes and algorithms developed by the team are made freely available on GitHub (https://github.com/procf) with tutorials provided on how to use each of the algorithms. The results have also been disseminated through conference and journal papers over the past two years and continue to be published on a timely fashion. PIs also plan to develop a unified data-center for the current work to be shared with the community upon completion of the project next year, with potential collaborative efforts.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The efforts in this project have been limited to foundational scientific explorations, with long ranging goals of additively manufacturing geopolymeric systems as structural components. Considering the complexity of geopolymeric materials, design cycle for them is extremely long, and as such the combined AI/Experiment/Computation approach taken here in compliance with MGI's mission will be effectively accelerating this design cycle far beyond just two-fold. The team is planning on proposing a follow on research and potential collaborative work with the Future Manufacturing team to see some aspects of the long range goals come to fruition.

Publications and References

1. D. Mangal, M. Nabizadeh, and S. Jamali, Predicting yielding in attractive colloidal gels, PRE, **109** (1), 014602 (2024)

2. D. Mangal, and S. Jamali, Role of interaction range on the microstructure and dynamics of attractive colloidal systems, Soft Matter, **20**, 4466-4473 (2024)

3. D. Mangal, R. Sanchez, S. Aime, and S. Jamali Small variations in particle-level interactions lead to large structural heterogeneities in colloidal gels, Soft Matter, **20**, 4692-4698 (2024)

4. M. Mahmoudabad, K. Kamani, S. Rogers, and S. Jamali, Unbiased construction of constitutive relations for soft materials from experiments via RhINNs, PNAS, **121** (2), e2313658121 (2024)

5. M. Saadat, D. Mangal, and S. Jamali, A rheologist's guideline to data-driven recovery of complex fluids' parameters, RSC Digital Discovery, **2**, 915 (2023)

6. M. Saadat, D. Mangal, and S. Jamali, UniFIDES: Universal Fractional Integro-Differential Equation Solvers, Eng. Appl. Artif. Intell., Under Review

7. M. Saadat, W. Hart, N. J. Wagner, and S. Jamali, Developing multi-fidelity platforms for data-driven constitutive meta-modeling of complex fluids, J. Rheology, in press

8. Smith, G. Donley, E. Del Gado & Zavala, Topological Data Analysis for Particulate Gels, , preprint 2024

9. Vinutha H. A. et al., Memory of flow in soft solids, , preprint 2024

NSF Network of Networks: Research and Education Accelerated by Connections in Clean Hydrogen (REACH2)

Lead Investigator: Jasna Jankovic, jasna.jankovic@uconn.edu
Participating Institutions: University of Connecticut, Fraunhofer ISE (Germany), LEPMI (France), Forschungszentrum Jülich (Germany)
Source of Support: NSF-OISE/AcellNet
Website: None
Keywords: Hydrogen, research, education, collaboration, international

This AccelNet Design Track project aims to form a global clean hydrogen Network of Networks (NoN) titled: Research and Education Accelerated by Connections in Clean Hydrogen (REACH2). The network will be composed of researchers from academia, national labs and industry, across the globe, with the goal to collaboratively address unmet fundamental research gaps and accelerate science in clean hydrogen technologies, such as water elecrolyzers and fuel cells, as well as to facilitate networking, education and training of next generation diverse talent.

Project Scope

REACH2 Network will focus on the following scientific objectives by facilitating coordinated and synergetic collaboration: (1) Study, develop, and implement process automation, advanced data science, ML and AI approaches in fabrication, testing, characterization, and data correlations for fuel cell and electrolyzer systems; (2) Accelerate scale-up fabrication science for these systems; (3) Enable rational design, synthesis and understanding of next generation highly-performing and stable catalysts and electrolytes for these systems; (4) The most important focus of REACH2 is to enable effective and systematic scientific exchange, sharing of ideas and knowledge, and synergistic training/education of next generation leaders in clean energy.

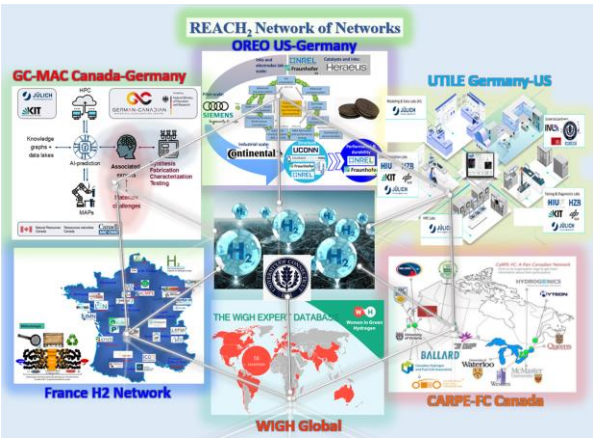


Figure 1. Global clean hydrogen Network of Networks (NoN): Research and Education Accelerated by Connections in Clean Hydrogen (REACH2).

Relevance to MGI

The proposed activities in REACH2 project are directly relevant to MGI strategic mission, by collaboratively providing, integrating, processing and delivering materials data in the domain of hydrogen fuel cells and electrolyzers. This scientific area is highly challenging and requires a huge amount of data, advanced facilities, diverse expertise, and excessive resources. To draw correlations, statistical data are needed, requiring hundreds of samples, thousands of characterization and testing data, and endless processing and correlations. No network has enough data, samples, time or expertise to satisfy those requirements. REACH2 will enable exactly that, rapidly advancing the science by combining our expertise, knowledge, facilities, data, materials and resources. We will combine fabrication, testing and characterization data, ML and AI approaches, and automation methods from the network members, and integrate them to accelerate discovery and advance common knowledge. In that way we will accelerate progress that is otherwise slow when a singular research center or network tries to address it.

Technical Progress

Our Planning Project has just been awarded (July 2024). We have already conducted the Kickoff meeting, formed the international Network Planning Committee and Network Advisory Board, as well as planned our first workshop in Sept 2024.

Future Plans

To achieve the Network Planning Goals during the Design phase of our network, we are planning to conduct the following synergistic activities:

(i) Preliminary planning activities will be conducted to recruit all NoN members, select the NoN Planning Committee and Advisory Board, set up needed logistics and organize the main networking activities (ii) and (iii).

(ii) Conduct three in-person networking and planning workshops:

1) Workshop REACH2 (Sept '24, US) with the objective to focus on the network Planning Goal 1: design network roadmap, logistics, plans and actions (Sept 2024 at the University of Connecticut, US).

2) Workshop REACH2 (March '25, German) with the objective to focus on the network Planning Goal 2: plan and design a suite of shared and publicly accessible tools and platforms for data sharing, storage and processing.

3) Workshop REACH2 (Set '25, Canada) with the objective to focus on the network Planning Goal 3: plan and design training programs for development of future workforce and next generation of experts and leaders.

(iii) Action periods after the workshops will be organized to allow for the international network teams to collaboratively work on the tasks defined during the workshops and materialize the plans.

Broader Impacts and Workforce Development

Our proposed global H2 network, REACH2, will have consequential impact on attaining net-zero goals. It will create a coordinated and organized global synergistic collaboration of experts in the field of clean H2 technologies, through networking activities, sharing of knowledge, facilities, and scientific data. This will accelerate scientific progress and support both industry and governments in the effort of achieving mass production of clean H2 at low cost, and its use for energy generation, transportation, manufacturing and chemical/industrial processes. Moreover, the network will focus on the development of next generation diverse leaders in clean energy, by facilitating scientific exchange, networking and coordinated training of students and early-career researchers, enabling extensive broadening of the network's impact. Special emphasis will be placed on underrepresented minorities and broadening participation, diversifying and growing our future workforce, urgently needed for the expanding field of clean energy. Creating our international REACH2 network will allow us to achieve both our scientific and workforce goals on a global level that will have great impact on the planet and will benefit society by achieving a clean energy future and mitigate climate change.

Data Management and Open Access

One of REACH2 main goals is to establish a suite of shared and publicly accessible collaborative and networking tools and platforms (e.g., expert database and platform for (meta) data sharing, storage, and processing/modeling) aided by ML and AI. These platforms will be based on existing or in-development approaches within the network members. The goal is to generate creative ways to collect, store, share and process a huge amount of research data that each network member has been generating (e.g. synthesis and fabrication parameters, microscopy images, testing data, modeling data), but has been unable to effectively share. This will accelerate science, which has been hindered by evaluating limited amount of data within an isolated team or a smaller network. Such a platform would facilitate sharing, correlating and converging of the (existing and future) data, enabling discovery of new transformative interpretations and acceleration of the science.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Through our collaborative efforts is materials discovery and understanding, through synthesis, characterization, testing, as well as AI and ML approaches, we envision generating thousands and thousands of data and information. We will then utilize a comprehensive and integrated platform for managing and analyzing this rapidly expanding datasets derived, with the aim to derive correlations, accelerate understanding and enable effective knowledge generation using advanced tools. We will leverage AI to identify key descriptors for structure-function relationships in energy materials. The platform's models are characterized by their generality and agnosticism, making them applicable to a variety of materials disciplines. This comprehensive approach is envisioned to ensure not only advances in the field of materials science, but also to sets a new standard for the analysis and application of data in energy materials research.

Publications and References

None yet.

Computational Discovery of Polymeric Membranes for Polar Solvent Dehydration

Lead Investigator: G. Kane Jennings, kane.g.jennings@vanderbilt.edu
Participating Institutions: Vanderbilt University and Heriot-Watt University
Source of Support: NSF-DMREF
Website: https://osf.io/eyt3j/
Keywords: polymer membranes, screening, molecular simulation, machine learning, data mining

Project Scope

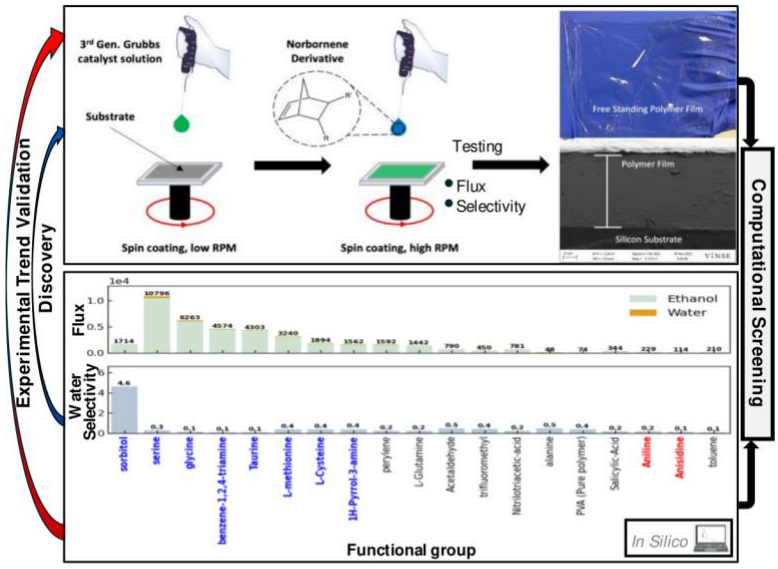


Figure 1. Schematic representation of the spin coating ring-opening metathesis polymerization (top panel) membrane fabrication and testing (top panel). Computational results used for experimental trend validation and discovery of new functional groups for future membrane fabrication (bottom panel).

The rational design of next generation membranes for solvent-solvent separations is a significant challenge, given the vast chemical design space. Through an integrated experimental and computational approach combined with machine learning, we are performing an Materials Genome Initiative (MGI)-inspired screening to transform the membrane development paradigm. This project is developing functionality- and performance-driven screening with close coupling between simulations and experiment to fabricate high-performance polymer membranes for targeted separations. Our work focuses on the dehydration of polar solvents by pervaporation where effective new materials can eliminate the need for costly, high-energy separations, while enabling effective solvent reuse for sustainable manufacturing.

Relevance to MGI

Figure 1 shows the integration between molecular simulations and materials synthesis for the discovery of new polymer membranes. We can rapidly make a vast array of polymers with general structures as shown in the top of Figure 1 via spin coating ring-opening metathesis polymerization (scROMP). Using molecular simulations, we can screen functional side chains (R and/or R') from this general structure to characterize properties such as density and fractional free volume (FFV), as well as dynamic aspects such as polymer chain mobility, H_2O/ethanol uptake, and swelling. Polymers with a high calculated product of water selectivity and overall flux from the simulations are recommended as candidate compositions for polymer thin film synthesis via scROMP in this first screening loop.

Technical Progress

Our technical progress includes important advances in the following areas:

(i) The scROMP process combines polymer synthesis and deposition to enable the fabrication of polymer selective layers on thin film composite membranes as large as 36 cm^2 in under 2 min with less than 0.5 mL of solvent. The polymers are well defined with molecular weights exceeding 200 kDa and PDI < 1.2.[1] Through modeling the scROMP process, we have determined the kinetic rate constants for the polymerization process. Through computational screening in combination with scROMP, we have identified many polymers that successfully dehydrate ethanol, as a model polar solvent of industrial importance.

(ii) We have shown that random copolymer films can be prepared by scROMP.[1] To minimize the use of perfluoroalkyl substances (PFAS), a random copolymer, poly(norbornene-(perfluorooctyl)norbornene) at only 2% fluorinated monomer, exhibits wettabilities that match the 100% semi-fluorinated homopolymer, due to a

dense, surface-segregated fluorocarbon layer at the outermost nm of the copolymer film. These surface-segregated copolymers enable us to separate sorption from diffusion in calculating membrane selectivity.

(iii) Semi-fluorinated selective layers made from poly(n-perfluoroalkylnorbornenes) (pNBFn) exhibit high selectivities for water over ethanol while minimally swelling in many solvents (manuscript to be submitted in July, 2024). A critical chain length of 8 leads to superior performance in water selectivity, correlating with the most hydrophobic and oleophobic surface, while exhibiting higher swelling in water than in ethanol.

(iv) For the first time, we have shown the ability to decouple sorption from diffusion to quantify and explain the high water selectivities in poly(vinyl alcohol) membranes.

(v) We have developed a systematic approach for modeling, testing, and characterizing diverse polymer membranes using molecular simulation. Coupled with experimental testing, this method has provided deep insights into polar solvent separation and led to the discovery of new membrane materials. By using computationally efficient surrogate models, we have highlighted the importance of structural properties and polymer chain mobility in determining membrane performance. Our preliminary findings suggest that polymer structure may be more significant than its solvent affinity in the separation process.

(vi) Several molecular models have been developed to probe different properties of the polymers/membranes that might affect the pervaporation efficacy, specifically their adsorption-selectivity and diffusion selectivity. The models were utilized to simulate a series of pNBFn membranes. The simulation results helped explain selectivity improvement when pNB is functionalized with perfluoroalkyl side chains, by providing insights into polymer-solvent affinity, solvent diffusion inside the membrane, and the membrane film-solvent interface. These models have been implemented as scalable workflows and are currently being implemented in a screening of the larger pool of pNBDAC membranes.

Future Plans

(i) Through combined computational screening, simulations, and experiments, determine the most effective amide-linked aromatic side chains for polar solvent dehydration.

(ii) Create a preliminary ML model that will use the data generated from molecular simulations of single polymer chains to reduce the computational-screening time, enabling faster discovery of new membrane materials.

(iii) Use scROMP to fabricate block copolymer films and films with distributed charge that can enhance the sorption of water over ethanol while enabling rapid diffusion of water.

(iv) Gain fundamental insight on membrane mechanism and performance by comparing a thick membrane to multiple thinner membranes.

(v) Develop a workflow to model the pervaporation process for screening potential membrane films identified from prior experimental-simulation screening loops.

(vi) Examine interdiffusion and diffusion of solvents in polymer membranes using molecular simulations to gain insight into the transport mechanism.

Broader Impacts and Workforce Development

The project is training five Ph.D., one M.S., and two B.E. students on the discovery of new membranes for liquid-liquid separations. One Ph.D. and one M.S. student who spent effort on this project have graduated in 2024. A high school student is currently serving a 5-week internship on this project. We are once again providing a short course on membranes for a class of 15 gifted high school students through the Vanderbilt Summer Academy.

Data Management and Open Access

To facilitate sharing and dissemination of data we have created a publicly accessible project on the Center for Open Science's OSF.io web portal (https://osf.io/eyt3j). OSF.io provides a central location for linking to content, including datasets on zenodo.com, and includes direct integration with GitHub.com, where our software is being developed, and figshare.com where we are posting preprints, presentations/posters, and detailed experimental data.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The integration of computational approaches to identify optimal polymer compositions along with a new membrane fabrication process and highly diverse polymer chemistry is enabling the rapid discovery of new materials for membrane separations. We filed a patent application on the scROMP process: G. K. Jennings and L. Prozorovska, "Polymer Film Preparation Using Cyclic Olefin Monomers," U.S. Application Number 17/583,370 that is in process and is being licensed by Dr. Prozorovska at Scale Materials. Our approach enables new membrane materials to be identified and tested at benchtop scale, with promising systems as candidates for scale up to industrial membranes.

Publications and References

1. Z. J. Parkerson, L. Prozorovska, M. P. Vasuta, T. D. Oddo, and G. K. Jennings, "Simultaneous Spin Coating and Ring-Opening Metathesis Polymerization for the Rapid Synthesis of Polymer Films," *ACS Applied Materials & Interfaces*, **16**, 16754-16766 (2024). DOI: https://doi.org/10.1021/acsami.4c00211

Combining first principles and data driven approaches for materials discovery

Lead Investigator: Aaron Kaplan, adkaplan@lbl.gov
Participating Institutions: Lawrence Berkeley National Laboratory, University of California Berkeley
Source of Support: DOE-BES (DE-AC02-05CH11231, Materials Project program KC23MP)
Website: https://next-gen.materialsproject.org/
Keywords: electronic structure, high-throughput, big data, machine learning

Project Scope

The Materials Project (MP) seeks to compute physical and chemical properties of all realizable materials, whether these have already been synthesized or are theoretically predicted. To do this, we rely on electronic structure methods, particularly density functional theory (DFT), to compute thermodynamic, elastic, and electronic materials properties. To run calculations in a high throughput scale sufficient for materials discovery, MP develops robust code packages for automated workflow orchestration.

Relevance to MGI

MP continues to be a leader in integrating electronic structure theory, high-throughput DFT computation, and big data storage / analysis. As our group contains experts in electronic structure methods and in materials science, we can rapidly assess the applicability of new electronic structure methods as they become available. This quickly provides an assessment to those developing the methods (such as new functionals in DFT). The current adoption of the r^{2}SCAN functional [1,2] for MP's materials discovery calculations was motivated by active partnerships with theoretical groups. More, results from MP can immediately inform experimentalists about the predicted stability of novel materials and guide choices regarding materials selection by physical and electronic properties. More, if those predictions fail to be experimentally realized, these can inform the computational team about deficits in their methods. Recently, an experimental partner of MP (A-Lab) found that many Ytterbium-containing compounds had incorrectly predicted stabilities. The cause of this error was methodological in the choice of pseudopotential used for DFT calculations, and resulted in a larger audit of the computational parameters used by MP. Thus we are able to improve our methods by providing feedback to theoreticians, and by receiving feedback from experimentalists.

Technical Progress

Over the past year, MP has executed a complete audit of its electronic structure computational workflows, ensuring that, e.g., the pseudopotentials employed in its DFT calculations accurately reproduce all-electron calculations. This is in preparation of a complete recompute of the MP database with the advanced r^{2}SCAN density functional, which represents a significant improvement in approximation over PBE+U (used in the majority of MP's calculations). r^{2}SCAN, without a Hubbard U, captures greater local chemical bonding information than PBE, and can describe more diverse types of chemical bonding relevant for exotic materials, such as the cuprates. To ensure that our DFT calculations pass rigorous validation, we have concurrently developed an extensive validation package (https://github.com/materialsproject/pymatgen-io-validation) which checks hundreds of computational parameters used in DFT calculations for consistency with MP calculations.

MP has identified two key areas to expand its database of 150,000 unique materials: ensuring consistent coverage with respect to experimental databases such as the ICSD, and incorporation of materials predicted to be stable by machine-learning models. We have recomputed electronic properties for almost 120,000 materials predicted to be stable by Google Deepmind's GNoME project. These materials are currently being incorporated into the core MP database, almost doubling its size.

As these novel materials can represent a distributional shift in chemical spaces and bonding, we have developed data-driven metrics for assessing how similar structures are to known, experimentally-synthesized materials. These metrics are based on the most recent release of the ICSD and encode local bonding information to rapidly assess

whether structures lie within a reasonable "distance" from known materials. We have applied these metrics to MP's DFT computed structures and to the GNoME structures.

Based on our benchmarking effort, we have developed a new standard workflow for generating training data for machine-learned universal interatomic potentials (UIPs) at a consistent level of DFT approximation. This workflow is currently being used to develop a DFT dataset to retrain extant UIPs co-developed by MP, such as MACE [3]. By adroit selection of training structures, we hope to more completely map the space of materials potential energy surfaces (MatPES) and reduce the data needed to train UIPs.

These efforts are underpinned by the recent atomate2 and jobflow software libraries co-developed by MP, which define the workflows used by MP. This permits external users to replicate MP calculations for their materials spaces of interest. We have also led development of ML UIP workflows in atomate2 to assess these burgeoning tools.

Future Plans

We will begin a complete recompute of MP with the r^2SCAN functional and revised numerical parameters this year. The recompute includes roughly 30,000 ordered materials from the ICSD determined to be missing from MP. We are also developing infrastructure to better host and disseminate data relevant to machine learning applications, especially interatomic potentials. This infrastructure will be prototyped with the MatPES project, and will include multiple layers of accessibility for those solely interested in training data, and for those with greater understanding of electronic structure methods. Non-electronic properties computed with ML UIPs may eventually be incorporated into a separate materials explorer to: improve coverage of properties that are challenging to compute in high-throughput with DFT, such as phonon dispersion; and to give coarser estimates of solid stability in underexplored and high-dimensional chemical spaces.

Broader Impacts and Workforce Development

The MP database currently has more than 500,000 registered global users. Group members often present seminars and workshops on MP's data and computational toolsets to external research groups. We have hosted a long-running seminar series where external researchers who work with MP data or software present to our global audience. Our team consistently engages with our user base through the matsci community forum, where users can ask questions about the MP software stack and data, as well as our github respositories' issues and pull requests.

Data Management and Open Access

MP is a consistent leader in FAIR data management practices. The core MP and user-contributed MPContribs (https://next-gen.materialsproject.org/contribs) databases are findable and accessible online through an open RESTful API (https://github.com/materialsproject/api). This API provides search, authorization, and authentication on both the underlying data and machine generated labels. Parsed electronic structure calculations are stored and served as JSON documents to enable tight integration with MP data production and workflow management. Machine-readable formats are also available depending on the data type (e.g., CIFs for structure data) to ensure interoperability. Our infrastructure supports data reuse by documenting the detailed provenance of data and ensuring a Creative Commons license for distribution. A web interface (https://next-gen.materialsproject.org/materials) built upon the API permits retrieval and visualization of materials data. To ensure long term data accessibility and security, MP its data on NERSC's HPSS tape archive and Amazon AWS S3's Open Data exchange platform.

Advancing Along the Materials Development Continuum and Partnerships to Translation

By expanding the scope of materials and their properties included in MP, we make it possible to explore new, under-explored, and high-dimensional chemical spaces for application-driven materials design. In the long term, we aim to cover more materials properties that may be of interest to experimentalists (especially elastic and phonon properties). We have an active collaboration with Google's GNoME project, which will result in a major broadening of MP's chemical space coverage. We strive to keep our data and software open and accessible.

Publications and References

1. J.W. Furness, A.D. Kaplan, J. Ning, J.P. Perdew, and J. Sun, Accurate and Numerically Efficient r^2SCAN Meta-Generalized Gradient Approximation, J. Chem. Phys. Lett. **11**, 8208 (2020). DOI: 10.1021/acs.jpclett.0c02405
2. R. Kingsbury, A.S. Gupta, C.J. Bartel, J. Munro, S. Dwaraknath, M. Horton, and K.A. Persson, *Performance comparison of r^2SCAN and SCAN metaGGA density functionals for solid materials via an automated, high-throughput computational workflow*, Phys. Rev. Mater. **6**, 013801 (2022).
3. I. Batatia *et al.*, *A Foundation Model for Atomistic Materials Chemistry*, arXiv:2401.00096 (2024). *Submitted.* DOI: 10.48550/arXiv.2401.00096
4. S. Vijay, M.C. Venetos, E.W.C. Spotte-Smith, A.D. Kaplan, M. Wen, and K.A. Persson, *CoeffNet: Predicting Activation Barriers Through a Chemically-Interpretable Equivariant and Physically Constrained Graph Neural Network*, Chem. Sci. **15**, 2923 (2024). DOI: 10.1039/D3SC04411D
5. G.C. Moore, M.K. Horton, A.D. Kaplan, S.M. Griffin, K.A. Persson, *Realistic Non-Collinear Ground States of Solids with Source-Free Exchange Correlation Functional*, arXiv:2310.00114 (2024). *Submitted*. DOI: 10.48550/arXiv.2310.00114
6. A.D. Kaplan and A. Ruzsinszky, *Revealing Quasi-Excitations in the Low Density Homogeneous Electron Gas with Model Exchange-Correlation Kernels*, J. Chem. Phys. **159**, 224112 (2023). DOI: 10.1063/5.0174165
7. B. Kanungo, A.D. Kaplan, C. Shahi, V. Gavini, and J.P. Perdew, *Unconventional Error Cancellation Explains the Success of Hartree-Fock Density Functional Theory for Barrier Heights*, J. Phys. Chem. Lett. **15**, 323 (2024). DOI:10.1021/acs.jpclett.3c03088
8. A.D. Kaplan, C. Shahi, R.K. Sah, P. Bhetwal, B. Kanungo, V. Gavini, and J.P. Perdew, *How Does HF-DFT Achieve Chemical Accuracy for Water Clusters?*, J. Chem. Theory Comput. *accepted, in press*. (2024). DOI: 10.1021/acs.jctc.4c00560

Atomically Precise Catalyst Design for Selective Bond Activation

Lead Investigator: Ayman M. Karim, amkarim@vt.edu
Participating Institutions: Virginia Tech, University of Delaware, University of Pennsylvania
Source of Support: NSF-DMREF
Keywords: Isolated metal single atom catalysts, physics-based descriptors, hydrodeoxygenation

Project Scope

The project is focused on designing catalysts consisting of supported isolated metal atoms using unconventional supports prepared by atomic layer deposition (ALD) and a computationally driven descriptor-based approach to navigate the vast material space. **Our central hypothesis** is that the properties of these catalysts can be modulated to surpass the selectivity and activity of conventional catalysts by changing the structure or composition of the support.

Relevance to MGI

Our team, Ayman Karim from Virginia Tech, John Vohs and Raymond Gorte from the University of Pennsylvania, and Dionisios Vlachos from the University of Delaware, aims to develop a conceptual framework centered on artificial intelligence (AI)- and multiscale modeling-based methodology (Figure 1) to build guiding principles that can be leveraged to predict highly active, stable, and selective metal-support compositions. The model predictions will guide the synthesis of single-metal atoms supported on novel, high surface area unconventional support materials (perovskites and spinels) by atomic layer deposition, followed by detailed characterization of their properties, catalyst evaluation, and model assessment and refinement. By uncovering physics-inspired descriptors and harnessing the capabilities of machine learning, our team aims to predict how the surface composition of the oxide support and the local cation environment at the metal site influence stability, activity, and selectivity. We will ensure a high chemical fidelity of our model, and hence its predictions, by precise synthesis using ALD and assessing the model predictions experimentally through multiple characterizations of the atomic structure, calorimetry of binding of adsorbates to the metal sites and their spectroscopic signatures and finally their catalytic properties. The outcome of this research will serve as a foundational methodology for designing new materials in silico.

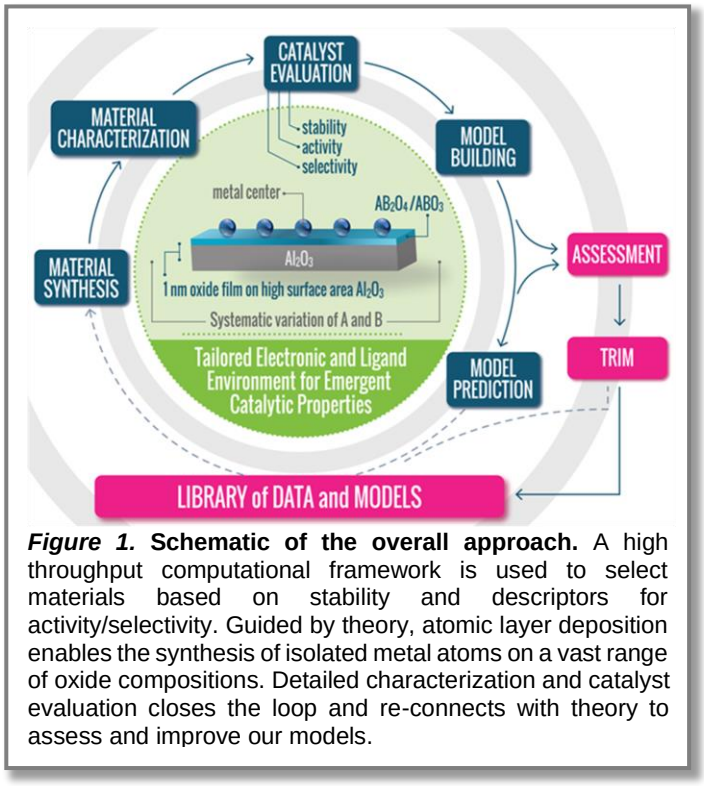


Figure 1. **Schematic of the overall approach.** A high throughput computational framework is used to select materials based on stability and descriptors for activity/selectivity. Guided by theory, atomic layer deposition enables the synthesis of isolated metal atoms on a vast range of oxide compositions. Detailed characterization and catalyst evaluation closes the loop and re-connects with theory to assess and improve our models.

Technical Progress

In the first ten months of the project, we focused on Rh, Ir and Pt single atoms supported on "simple" conventional metal oxides (Al_2O_3, TiO_2 and CeO_2), as model systems to benchmark our theory and experiments. We developed a modified ALD method for the deposition of isolated single metal atoms of Rh, Pt and Ir on Al_2O_3 and TiO_2. The stability, structure and spectroscopic signature of adsorbed CO predicted by our theoretical models agrees with our experimental results. Figure 2a shows an aberration-corrected scanning transmission electron microscopy image of Ir on Al_2O_3 where isolated single atoms can be clearly seen (similar results for Rh and Pt, not

shown). Figure 2b shows X-ray absorption spectra of Pt/Al_2O_3 where the oxidation state of Pt is close to that predicted by theory. Additionally, Figure 2c shows an infrared spectrum of of CO adsorbed on isolated Rh atoms on Al_2O_3 where the symmetric and asymmetric C-O vibrations of $Rh_1(CO)_2$ can be clearly seen. The work shows the facile and generality of our modified ALD synthesis method and will be submitted soon.

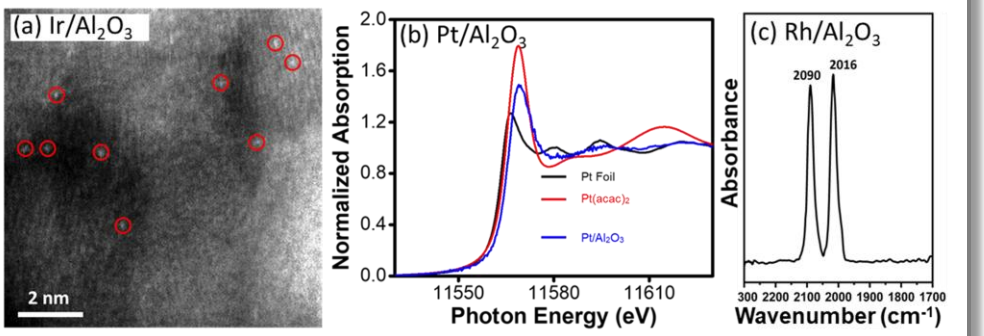


Figure 2. **Metal single atoms on Al_2O_3. (a)** Aberration-corrected STEM image of Ir/Al_2O_3. (b) L_3-edge X-ray absorption near edge structure spectrum of Pt/Al_2O_3 compared to $Pt(acac)_2$ and Pt foil. **(c)** DRIFTS of CO adsorbed on Rh/Al_2O_3.

Future Plans

Based on the initial agreement between our model and experimental results, we plan to expand the work to the catalytic studies of the model single metal oxides to benchmark the experimental kinetics to those calculated from our models for water-gas-shift and for hydrodeoxygenation of cresol reactions. After assessing and revising our models as needed, we will transition to thin films of single metal and mixed metal oxides which offer a vast structural and composition space that is ideal for theoretical investigation. By combining a gamut of analytical tools (e.g., density of states, Bader analysis, Mulliken spin polarization, computational IR and Raman spectroscopy) we are currently exploring electronic descriptors to predict the stability of single atoms on a variety of supports. We successfully synthesized thin films of binary oxides and we plan on continuing to synthesize a library of mixed thin film metal oxides guided by predictions from our modeling efforts and to assess their properties and their effect on the properties of the supported isolated atoms of Rh and Ir.

Broader Impacts and Workforce Development

The project is inherently multidisciplinary and to ensure that each student gains expertise in all its aspects (*i.e.*, materials synthesis and characterization, kinetics measurements, and multiscale modeling), we have bi-weekly virtual meetings and will implement a **rotation program** where each graduate student does a 1-to-2-month internship in the other PI's groups. Additionally, our groups will individually recruit UG students for research over the summers. For example, UD has two female graduate students and several undergraduates working full-time in this program. Lastly, UD will hold in person AI/ML modelling workshops for high school students led by a graduate student on alternating years between UD and VT which will also be made available online for remote access to UPenn.

Data Management and Open Access

The computational data will be stored in a state-of-the-art database [S. M. Lambor, S. Kasiraju, and D. G. Vlachos, An Extensible and FAIR Data Management Framework and Datahub for Multiscale Modeling in Heterogeneous Catalysis, *J. Chem Inf. Model.* **63**(14), 4342-4354 (2023). DOI:10.1021/acs.jcim.3c00123]. We will make all data available in a well-documented, easily accessible format. The experimental data will be made available through our published manuscripts.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The computational methods and approaches could be adopted by various companies that practice materials synthesis and software development.

Publications and References

1. Shen, Lu, Satyana, Caratzoulas, Vlachos, Karim, Gorte and Vohs, to be submitted.
2. George Yan, Salman A. Khan, Dionisios G. Vlachos, Charge Transfer Drives Hydrogen Adsorption, Spillover, and Hydroxylation at the $Pt/\gamma\text{-}Al_2O_3$ Interface, Revision under Review.
3. George Yan, Dionisios G. Vlachos, Impact of Metal Clusters on the Lewis Acidity of Oxide Surfaces: First Principles Calculations of $Pt_{10}/\gamma\text{-}Al_2O_3(110)$, Submitted.

Closed-Loop Design of Polymers with Adaptive Networks for Extreme Mechanics

Lead Investigator: Chenfeng Ke, cke@wustl.edu
Participating Institutions: Washington University in St. Louis, Boston University, The University of California, Berkeley, the University of Chicago, and the University of Texas at Dallas
Source of Support: NSF-DMREF
Website: https://www.adaptex.org/
Keywords: adaptive polymer network, extreme mechanical property, high throughput synthesis, machine learning, self-driving lab

Project Scope

This project aims to produce mechanically robust polymers with slide-ring and dynamic covalent networks through a closed-loop integration of simulation, synthesis, characterization, and modeling. We will establish an accelerated materials discovery loop using multiscale computational simulation, high-throughput polymer synthesis, large-scope materials characterization, and machine learning-based materials re-design. A key feature is using 3D-printing as a discovery tool for rapidly studying formulations and processing conditions. This collaboration will create polymers with outstanding mechanical properties such as high Young's modulus, strength, high fatigue resistance, good self-healing ability, and high stretchability for applications in flexible sensors, soft actuators, robotics, and energy harvesting devices.

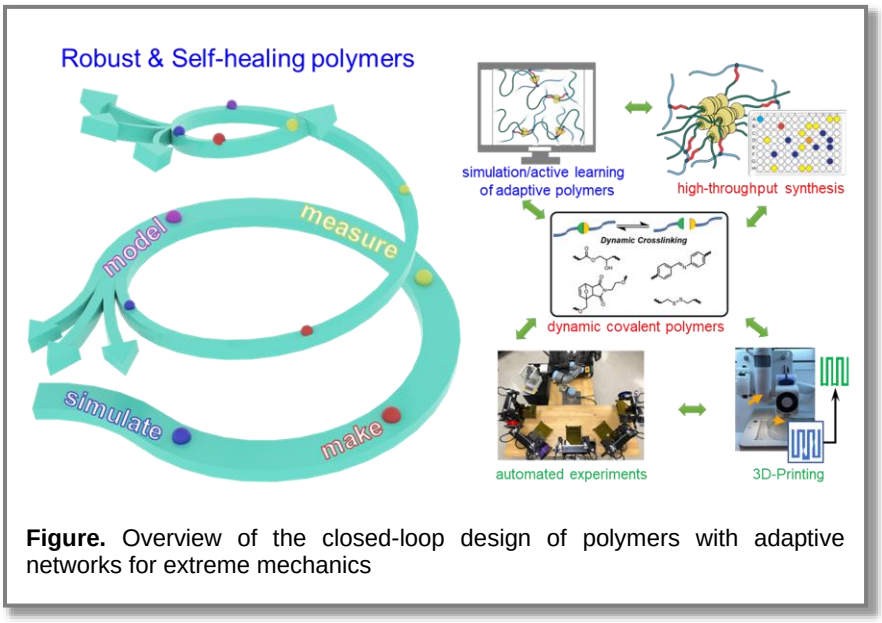


Figure. Overview of the closed-loop design of polymers with adaptive networks for extreme mechanics

Relevance to MGI

The development of the proposed mechanically robust adaptive polymer networks will be integrated into an iterative materials discovery loop (Figure). First, the design of polymers will be guided by hierarchical simulations. Next, the discovery of these polymers will be accomplished and accelerated by high-throughput synthesis and automated experiments. Then, the generated experimental data set will be fed back into a physics-informed active learning process for property optimization and discovery. In addition, we will introduce 3D printers as mechanical property validation tools and platforms to test the manufacturability of the discovered materials.

Technical Progress

Starting with simulation-guided polymer network design, the Ferguson lab developed an all-atom molecular model of double-threaded PEG chains through a γ-cyclodextrin ring in explicit solvent. Preliminary proof-of-principle molecular dynamics simulations of slide ring behavior were conducted in the iso-strain and iso-tension ensembles. Currently, enhanced sampling calculations are being undertaken to quantify the thermodynamic landscape for ring sliding along the chains as a function of tension and curvature, aligning with experimental measurements by the Ke lab. Experimentally, the Ke lab synthesized a series of ketoenamine-crosslinked

cyclodextrin-based hydrogels with highly mechano-responsive characteristics such as high toughness and fatigue resistance by introducing crystalline domain-crosslinked polyrotaxane networks. Mechanical training revealed that these hydrogels possess exceptional mechanical features, including a Young's modulus of 4.3 MPa, strength of 8.4 MPa, fracture energy of 13.2 kJ/m², and a fatigue threshold of 770 J/m², marking them among the best mechanically trained hydrogels reported. The Gu lab utilized these viscoelastic hydrogels for direct-ink-write 3D printing, optimizing parameters such as extrusion pressure and infill density to achieve scalable and rapid printing at 10 mm/s. Meanwhile, the Smaldone lab fabricated 3D printable filaments containing dynamic polyester networks designed to reduce mechanical anisotropy introduced during filament printing. Collaborating with the Smaldone lab, the Brown lab developed an autonomous testing process for integration with the synthesis pipeline. This includes an automatic system for evaluating print performance and selecting processing conditions to enhance printing, as well as a three-point bending process for assessing the non-linear mechanics of additively manufactured polymers. This process will evaluate the strengthening effect of dynamic crosslinks in polymers produced by fused filament fabrication.

Future Plans

The Ferguson group will study the influence of chemical modifications to the ring and chains upon the thermodynamic and kinetic behaviors, while the Ke and Gu labs will focus on optimizing the synthesis and fabrication of polyrotaxane hydrogels through closed-loop design. The Ke group plans to implement high throughput hydrogel synthesis to expand the materials library through a copolymerization approach. During 3D printing, imaging data will be collected (with sensors) by the Gu group throughout the fabrication process to inform machine-learning algorithms that can enable auto-calibration of the optimized printing settings for printing the hydrogel-based materials. The Smaldone group plans to integrate dynamic polymer networks into polyrotaxane networks to create double-network polymers with significantly enhanced mechanical properties. The Brown lab will test samples provided by the Smaldone group to evaluate how these chemical features affect the path dependence of material properties. We are also implementing smart spools to track filament properties during printing.

Broader Impacts and Workforce Development

Through collaboration among five institutions, we plan to create a dynamic outreach and workforce development program that integrates computational and experimental work. Currently, this project supports five PhD students. All PIs and junior researchers meet monthly on Zoom to present research updates from each lab. Additionally, the team has begun developing a polymer knowledge playlist, which will be assembled and published on the DMREF project website. We also plan to develop a virtual seminar series where junior researchers on the team will present their results. These talks will be open to other DMREF teams. PI Gu hosted a 3D printing workshop for underrepresented undergraduates (25 participants) where students had an opportunity to build a 3D printer, learn CAD skills, and participate in a design challenge.

Data Management and Open Access

The shared digital research data will benefit the polymer materials development and 3D-printing industries, as well as serve as educational resources for preparing the next-generation workforce. These data will be hosted on the MDF, an online data repository that associates rich metadata with datasets, mints DOIs, and ensures data is searchable in compliance with FAIR principles. The data will be referenced within published research articles and presentations using their permanent DOIs.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Our project aims to deliver a series of high-performance hydrogels and plastics. Their biocompatibility will allow their use as tissue engineering scaffolds or artificial tissue replacements. We anticipate filing several patent applications during the funding period. In collaboration with the Washington University Office of Technology Management, we plan to identify potential industry partners for technology transfer to the private sector.

Publications and References

No publications have been submitted since it is year 1 of the project. The lead PI will present the preliminary results at a Gordon Research Conference in Multiscale Mechanochemistry and Mechanobiology in July 2024.

Center for Predictive Simulation of Functional Materials

Lead Investigator: Paul Kent, kentpr@ornl.gov
Participating Institutions: Oak Ridge National Laboratory, Sandia National Laboratory, Argonne National Laboratory, North Carolina State University, Brown University
Source of Support: DOE BES
Website: Project - https://cpsfm.ornl.gov, Simulation codes - https://qmcpack.org
Keywords: Condensed Matter, First-Principles/Ab Initio Calculations, Quantum Materials, Electron Correlation

Project Scope

The Center for Predictive Simulation of Functional Materials develops, validates, and distributes external-parameter-free methods and open-source codes to accurately predict and understand the properties of functional and quantum materials with strong electronic correlations, van der Waals interactions, and spin-orbit interactions. The primary focus is Quantum Monte Carlo (QMC) techniques and the open source QMCPACK code (https://qmcpack.org). Distinct from other methods, the size of the few approximations in QMC can be quantified. The capabilities allow predictions to be made where approximate-in-practice approaches such as density functional theory are not reliable enough. They can also serve as benchmarks in materials databases, for machine learning, and for informing more approximate theoretical methods.

Relevance to MGI

This project focuses on fundamental theoretical developments, their implementation, and subsequent validation to perform accurate and reliable predictions of materials properties at the quantum mechanical level. Emphasis is placed on materials and properties where existing methods are either inadequate and unable to capture the underlying physics or where additional accuracy is desired. In quantum materials, the combination of strong electronic correlations, spin-orbital effects, magnetism, and their interactions with the underlying lattice can result in novel properties of interest both fundamentally and for possible technological applications. For example, in magnetic topological materials existing density functional approximations are claimed not to reliably reproduce the magnetic space group, necessitating the use of more accurate approaches to down select the most promising materials for synthesis. To meet this challenge, we are systematically developing the theoretical and computational toolchains needed to apply QMC to these materials, and to make these tools openly available and accessible. Our developments in spin-orbit and effective core potentials now enable QMC to be applied to materials such as $MnBi_2Te_4$ [13] and the 4*f* element bearing $TbMn_6Sn6$ [12].

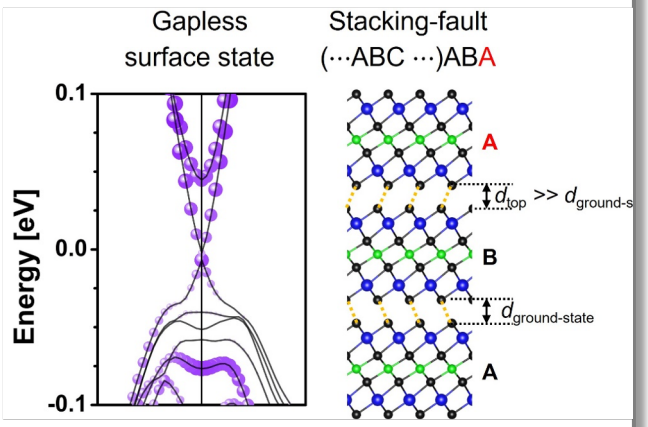


Figure 1. By advancing Quantum Monte Carlo methods to where they could be applied to complex quantum materials such as $MnBi_2Te_4$ (MBT), we found [13] that a gapless surface state with non-trivial topological properties can result solely from stacking-fault disorder in MBT. This highlights the significant role of interlayer separation as a determinant of interlayer coupling, band structure, and topology, and suggests new routes for realization of topological materials. (Left) MBT surface gap closure due to near surface stacking faults. (Right) Near surface stacking fault geometry. A greater interlayer separation near the surface redistributes charge as the band inversion nearly reverses at gap closure.

Technical Progress

We have made significant progress in extending the reach and accuracy of QMC approaches, in analyzing the results, and improving automation. For example, (i) Correlation consistent effective core

potentials/pseudopotentials (ccECPs) have been developed for a wider range of elements including Gd and Tb [4,6,15]; (ii) New implementations of orbital optimization promise to reduce the dependence of QMC on input trial wavefunctions, increasing accuracy and facilitating application to systems where mean-field approaches are highly questioned; (iii) We have developed methods to obtain reaction barriers within QMC by using extensions of our surrogate Hessian technique [20]; (iv) QMCPACK has been developed for Exascale and is now able to run on laptops through to NVIDIA, AMD, and Intel GPU accelerated systems such as Perlmutter, Frontier, and Aurora, respectively. These developments enable new applications of QMC on very topical materials such studies of the role of spin-orbit coupling on layered materials such as $RuCl_3$[5] (a proposed realization of the Kitaev spin liquid), and studies of magnetism and topology in $TbMn_6Sn6$ [12] and $MnBi_2Te_4$ [13]. Based on the reliability realized in high throughput workflows of small molecular systems [8] for machine learning applications, we are now extending the methodology to encompass the significantly more challenging and computationally expensive solids.

Future Plans

We plan to develop methods, code, and data that will result in a leap forward in the scientific capabilities of Quantum Monte Carlo (QMC) methods, as well as initial research demonstrations. These advances are needed for materials where combinations of strong electronic correlations, van der Waals interactions, and spin-orbit interactions give rise to properties of interest for potential energy applications and at the same time also challenge established theoretical and computational approaches. Algorithmic improvements will result in increased robustness of computational workflows, aiding wider use including by automated AI and machine-learning based approaches. Our methods will be made available through validated open-source codes, with examples, documentation, and training provided through workshops and video tutorials.

Broader Impacts and Workforce Development

While research results are conveyed through traditional publications, training in the developed methods and tools is facilitated through user workshops, both in-person/hybrid and purely virtual. Recordings are provided on the QMCPACK YouTube channel. Recognizing requests from the community, a tutorial paper "a practical guide to Quantum Monte Carlo" is currently in development. Besides training in condensed matter, students and postdocs also receive training in modern research scientific computing and software development. On graduating or leaving the project, to-date all participants have successfully found immediate employment at National Laboratories, as tenure track faculty, and at both startup and established companies in the scientific sphere.

Data Management and Open Access

FAIR (findable, accessible, interoperable, and reusable) principles are fully implemented, including for software source codes, and experimental and computational data. QMCPACK is developed fully open source at https://github.com/QMCPACK/qmcpack, with direct access to the latest development version and all versioned releases. Documentation is provided online first via https://qmcpack.readthedocs.io. We have expanded our ccECPs to new elements and provide these via https://pseudopotentiallibrary.org. ccECPs are seeing use beyond QMC, including in quantum chemistry and in neural network approaches. Data from individual studies is submitted to https://materialsdatafacility.org/. New projects computing properties of materials series will be submitted to community databases and we will request support for statistical error bars where support is currently lacking.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We are delivering theories, methods and open-source software implementations able to produce reliable predictions of materials structure and properties for classes of materials where we either currently lack reliable methods or where greater accuracy is called for. Development of automated workflows adapted for Monte Carlo and statistically based methods will enable their wider use. We plan to supplement existing open computational materials databases with benchmark data for these classes of material and property, and also for systems requested by the community. An important aspect of this work will be collaborating with developers of materials databases to provide data in appropriate formats and with sufficient provenance [18] and to develop coordinated roadmaps with developers of other electronic structure methods [19].

Publications and References

20 selected recent publications:

1. P. R. C. Kent, A. Annaberdiyev, A. Benali, M. Chandler Bennett, E. Josue Landinez Borda, P. Doak, K. D. Jordan, J. T. Krogel, I. Kylanpaa, J. Lee, Y. Luo, F. D. Malone, C. A. Melton, L. Mitas, M. A. Morales, E. Neuscamman, F. A. Reboredo, B. Rubenstein, K. Saritas, S. Upadhyay, H. Hao, G. Wang, S. Zhang, and L. Zhao. *"QMCPACK: Advances in the development, efficiency, and application of auxiliary field and real-space variational and diffusion Quantum Monte Carlo"*, Journal of Chemical Physics **152** 174105 (2020). DOI: 10.1063/5.0004860
2. C. Bennett, G. Hu, G. Wang, O. Heinonen, P. R. C. Kent, J. T. Krogel, and P. Ganesh, *"Origin of Metal-Insulator Transitions in Correlated Perovskite Metals"*. Physical Review Research Letters **4** L022005 (2022). DOI: 10.1103/PhysRevResearch.4.L022005
3. E. B. Isaacs, H. Shin, A. Annaberdiyev, C. Wolverton, L. Mitas, O. Heinonen "Assessing the accuracy of compound formation energies with quantum Monte Carlo", Physical Review B **105** 224110 (2022). DOI: 10.1103/PhysRevB.105.224110
4. G. Wang, B. Kincaid, H. Zhou, A. Annaberdiyev, M.C. Bennett, J.T. Krogel, and L. Mitas, "A new generation of effective core potentials from correlated and spin-orbit calculations: selected heavy elements", J. Chem. Phys. **157** 054101 (2022). DOI: 10.1063/5.0087300
5. A. Annaberdiyev, C. A. Melton, G. Wang, and L. Mitas, "*Electronic structure of α–$RuCl_3$ by fixed-node and fixed-phase diffusion Monte Carlo methods"*, Physical Review B **106** 075127 (2022). DOI: 10.1103/PhysRevB.106.075127
6. B. Kincaid, G. Wang, H. Zhou, and L. Mitas, *"Correlation consistent effective core potentials for late 3d transition metals adapted for plane wave calculations"*, J. Chem. Phys. **157** 174307 (2022). DOI: 10.1063/5.0109098
7. Q. Zhang, G. Hu, V. Starchenko, G. Wan, E. M. Dufresne, Y. Dong, H. Liu, H. Zhou, H. Jeen, K. Saritas, J. T. Krogel, F. A. Reboredo, H. N. Lee, A. R. Sandy, I. C. Almazan, P. Ganesh, and D. D. Fong, *"Phase transition dynamics in a complex oxide heterostructure"*, Physical Review Letters **129** 235701 (2022). DOI: 10.1103/PhysRevLett.129.235701
8. B. Huang, O. A. von Lilienfeld, J. T. Krogel, and A. Benali, *"Towards DMC accuracy across chemical space with scalable Δ-QML"*, J. Chemical Theory and Computation **19** 1711 (2023). DOI: 10.1021/acs.jctc.2c01058
9. T. Ichibha, K. Saritas, J. T. Krogel, Y. Luo, P. R. C. Kent, and F. A. Reboredo. *"Existence of La-site antisite defects in $LaMO_3$ (M = Mn, Fe, and Co) predicted with many-body diffusion quantum Monte Carlo"*, Scientific Reports **13** 6703 (2023). DOI: 10.1038/s41598-023-33578-1
10. T. Ichibha, S. Yoon, J. M. Ok, M. Yoon, H. N. Lee, and F. A. Reboredo, *"Thermodynamic understanding of impurity phase segregation in a $PdCrO_2$/$CuCrO_2$ Heterostructure"*, Advanced Physics Research (2023). DOI: 10.1002/apxr.202200080
11. M. Brahlek, A. R. Mazza, A. Annaberdiyev, M. Chilcote, G. Rimal, G. Halász, A. Pham, Y.-Y. Pai, J. T. Krogel, J. Lapano, H. N. Lee, B. J. Lawrie, G. Eres, J. McChesney, T. Prokscha, A. Suter, S. Oh, J. W. Freeland, Y. Cao, J. S. Gardner, Z. Salman, R. G. Moore, P. Ganesh, T. Z. Ward. *"Emergent magnetism with continuous control in an ultrahigh conductivity layered oxide"*, Nano Letters **23** 7279 (2023). DOI: 10.1021/acs.nanolett.3c01065
12. A. Annaberdiyev, S. Mandal, L. Mitas, J. Krogel, P. Ganesh, *"The role of electron correlations in the electronic structure of putative Chern magnet $TbMn_6Sn_6$ using correlated methods"*, npj Quantum Materials **8** 50 (2023). DOI: 10.1038/s41535-023-00583-6

13. J. Ahn, S.-H. Kang, M. Yoon, P. Ganesh, and J. T. Krogel, *"Stacking Faults and Topological Properties in $MnBi_2Te_4$: Reconciling Gapped and Gapless States"*, Journal of Physical Chemistry Letters **14** 9052 (2023). DOI: 10.1021/acs.jpclett.3c01939
14. H. Shin, P. Ganesh, P. R. C. Kent, A. Benali, A. Bhattacharya, H. N. Lee, O. Heinonen, J. T. Krogel, *"DFT+U and Quantum Monte Carlo study of electronic and optical properties of $AgNiO_2$ and $AgNi_{1-x}Co_xO_2$ delafossite"*, Physical Chemistry Chemical Physics **26** 6967 (2024).10.1039/D3CP03477A
15. H. Zhou, B. Kincaid, G. Wang, A. Annaberdiyev, P. Ganesh, L. Mitas, *"A new generation of effective core potentials: selected Lanthanides and heavy elements"*, J. Chem. Phys. **160** 084302 (2024). DOI: 10.1063/5.0180057
16. A. Annaberdiyev, P. Ganesh, J. Krogel, *"Enhanced twist-averaging technique for magnetic metals: applications using Quantum Monte Carlo",* Journal of Chemical Theory and Computation **20** 2786 (2024). DOI: 10.1021/acs.jctc.4c00058
17. D. Staros, B. Rubenstein, and P. Ganesh. *"A First-Principles Study of Bilayer 1T'-WT_2/CrI_3: A Candidate Topological Spin Filter".* NPJ Spintronics **2** 4 (2024). DOI: 10.1038/s44306-023-00007-y
18. K. Choudhary, D. Wines, K. Li, K. F. Garrity, V. Gupta, A. H. Romero, J. T. Krogel, K. Saritas, A. Fuhr, P. Ganesh, P. R. C. Kent, K. Yan, Y. Lin, S. Ji, B. Blaiszik, P. Reiser, P. Friederich, A. Agrawal, P. Tiwary, E. Beyerle, P. Minch, T. D. Rhone, I. Takeuchi, T. B. Wexler, A. Mannodi-Kanakkithodi, E. Ertekin, A. Mishra, N. Mathew, S. G. Baird, M. Wood, A. D.e Rohskopf, J. Hattrick-Simpers, S.-H. Wang, L. E. K. Achenie, H. Xin, M. Williams, A. J. Biacchi, and F. Tavazza, *"JARVIS-Leaderboard: A Large Scale Benchmark of Materials Design Methods",* npj Computational Materials 10 93 (2024). DOI: 10.1038/s41524-024-01259-w
19. V. Blum, R. Asahi, J. Autschbach, C. Bannwarth, H. Bernhard Schlegel, G. Bihlmayer, S. Blugel, L. A. Burns, T. Daniel Crawford, W. Dawson, W. Albert de Jong, C. Draxl, C. Filippi, L. Genovese, P. Giannozzi, N. Govind, S. Hammes-Schiffer, J. R. Hammond, B. Hourahine, A. Jain, Y. Kanai, P. R. C. Kent, A. H. Larsen, S. Lehtola, X. Li, R. Lindh, N. Makri, S. Maeda, J. Moussa, T. Nakajima, J. A. Nash, M. J. T. Oliveir, P. D. Patel, G. Pizzi, G. Pourtois, B. P. Pritchard, E. Rabani, M. Reiher, L. Reining, X. Ren, M. Rossi, N. Seriani, L. V. Slipchenko, A. J. W. Thom, E. F. Valeev, B. Van Troeye, L. Visscher, V. Vlcek, H.-J. Werner, D. B. Williams-Young, T. L. Windus. *"Roadmap on Methods and software for electronic structure based simulations of chemistry and materials"*, Accepted in Electronic Structure (2024). DOI: 10.1088/2516-1075/ad48ec
20. G. Iyer, N. Whelpley, J. Tiihonen, P. Kent, J. Krogel, B. Rubenstein. *"Force-Free Identification of Minimum-Energy Pathways and Transition States for Stochastic Electronic Structure Theories"*, Submitted to Journal of Chemical Theory and Computation (2024). DOI: 10.48550/arXiv.2402.13189

Computationally Driven Discovery and Synthesis of 2D Materials through Selective Etching

Lead Investigator: Konstantin Klyukin
Participating Institutions: Auburn University, University of Arizona, Missouri S&T, Tuskegee University
Source of Support: NSF-DMREF
Website: none
Keywords: 2D materials, MXenes, selective etching, molecular dynamics

Project Scope

The overarching objective of this project is to accelerate the discovery of novel 2D materials with diverse compositions through systematic studies and fundamental understanding of the factors governing the successful synthesis using electrochemical etching (E-etching). This process is based on applying an electric potential to metal or semiconductor surfaces separated by an electrolyte solution, which causes the surface to dissolve in a controlled manner.

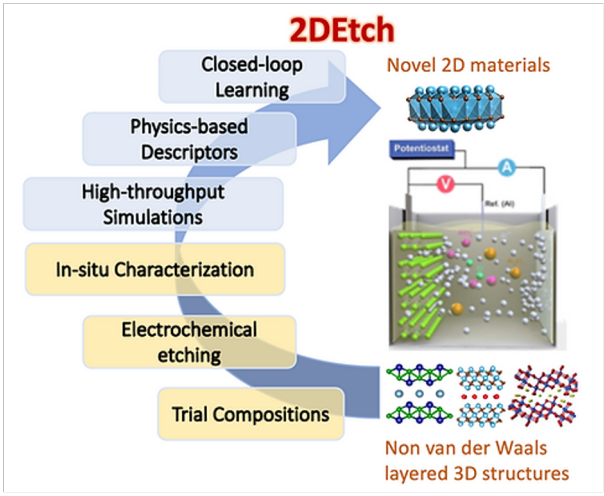


Figure. The research scope integrates hypothesis-driven computational and experimental methods to discover a large pool of 2D materials that can be obtained through selective etching

Relevance to MGI

Our goals will be achieved through a detailed characterization and closed-loop integration of experimental and computational methods. We suggest that broadening the pool of synthetically realizable materials is possible through a detailed understanding of all the stages of the materials synthesis, from the selection of precursors to consideration of all possible reactions during the synthesis and investigation of the stability of final products under etching conditions. The development of computational predictive models based on the rationale of E-etching processes and their continuous calibration using experimental data is a crucial part of this DRMEF program. The conversion of MAX phases to MXene will serve as a template to develop our E-etching process and predictive model, which can be subsequently employed to discover novel 2D materials derived from other 3D structures.

Technical Progress

The development of our project is still in its early stages, our groups are currently focused on the development and validation of simulations and experimental loops. The experimental team designed and built electrochemical cells enabling *in situ* monitoring of reaction products and demonstrated their capabilities to study etching of Ti_3AlC_2 MAX phase to produce high-quality $Ti_3C_2T_x$ MXenes (T_x = O/OH/F). Current cell is designed for *in situ* Raman spectroscopy analysis to detect gaseous reaction products and monitor kinetics of etching. Next cell design will also allow the collection of evolved gases for their analysis by gas chromatography

Our recent computational results shed light on the factors governing the extraction of Ti atoms from $Ti_3C_2T_x$ (i.e., degradation of $Ti_3C_2T_x$). We demonstrated that the kinetics of Ti atom release is strongly correlated with the descriptive properties of $Ti_3C_2T_x$ surface, such as Ti vibrational modes and work function. [1] Current computational efforts are focused on a detailed understanding of factors that can limit the etching of Ti_3AlC_2 and similar MAX phases. We investigate the behavior of Ti_3AlC_2 under electrochemical conditions and calculate the kinetics of rate-limiting steps such as extraction and diffusion of Al and Ti atoms.

Future Plans

Our next objective will be to connect experimentally measured parameters indicating successful or unsuccessful etching to energy landscapes calculated from the first principles and determine the key thermodynamic and kinetic

parameters that govern the synthesis of MXenes through the e-etching of MAX phases. Building on these outcomes, we will next attempt to determine the synthesizability of a broad range of MAX phases and other layered 3D non-van der Waals compounds and identify the optimal parameters for their E-etching (i.e., electrolyte, potential, etc.).

Broader Impacts and Workforce Development

Klyukin and Malone, along with other faculty members at Auburn University, worked together to establish the Center for Multiscale Modeling of Materials and Molecules (CM^4) between Auburn and Tuskegee Universities. The primary goal of our initiative is to develop the next generation of workforce in computational materials and molecular sciences. This involves creating new curricula, coordinating interdisciplinary seminar series, and initiating outreach activities for K-12 community in southeast Alabama.

All project PIs initiated the development of an introductory "Data-driven Materials Design" module, which will be further incorporated into various science, technology, engineering, and mathematics (STEM) at Auburn, Tuskegee, Missouri S&T, and University of Arizona.

Data Management and Open Access

A long-term goal of this project is to establish a searchable database containing computational and experimental data for materials that can be produced via selective electrochemical etching. Ascribing FAIR principles, we will also publish computational and experimental data in open data repositories:
V. Nesterova, V. Korostelev, K. Klyukin, Konstantin (2024). Ti3C2T2.zip. figshare. Dataset. https://doi.org/10.6084/m9.figshare.25236772.v1

Advancing Along the Materials Development Continuum and Partnerships to Translation

The proposed research will introduce a process for the synthesis of high-quality MXenes and other 2D materials with different compositions and structures. At the later stage of our project, we are going to explore the possibility of scaling up the production of MXenes and/or other 2D materials by designing innovative electrochemical cells capable of handling large quantities of precursors and providing extended capabilities for multi modal *in situ* reaction monitoring. The outcomes of this research also have the potential to expand the family of stable 2D materials with superior properties for various applications.

Publications and References

1. V. Nesterova, V. Korostelev, K. Klyukin, *"Unveiling the role of termination groups in stabilizing MXenes in contact with water."* Journal of Physical Chemistry Letters, 15, **13**, 3698–3704 (2024) DOI: 10.1021/acs.jpclett.4c00045

Electrocatalysis Consortium (ElectroCat): A DOE Energy Materials Network (EMN) Consortium

Poster Presenter: Wilton J. M. Kort-Kamp (kortkamp@lanl.gov)
Lead Investigators: Piotr Zelenay (zelenay@lanl.gov), Deborah Myers (dmyers@anl.gov)
Participating Core Institutions: Argonne National Laboratory, Los Alamos National Laboratory, National Renewable Energy Laboratory, Oak Ridge National Laboratory
Website: https://www.electrocat.org/
Keywords: energy, hydrogen, fuel cell, electrolyzer, electrocatalyst

Project Scope

The ElectroCat (Electrocatalysis) Consortium is aimed at increasing U.S. competitiveness in developing and manufacturing fuel cell and water electrolyzer energy conversion devices by addressing primary challenges to the widespread implementation of these technologies. The platinum group metal (PGM) electrocatalysts that are the current standard in low-temperature fuel cell and water electrolyzer systems are expensive and restrict the ability to be cost-competitive with traditional hydrocarbon-based technologies (e.g., internal combustion engine and steam methane reforming, respectively). In this sense, catalyst design represents the most pressing material barrier related to fuel cell and water electrolyzer deployment. ElectroCat is addressing this barrier by accelerating the development and deployment of platinum group metal-free (PGM-free) electrocatalysts in low-temperature fuel cells and water electrolyzers.

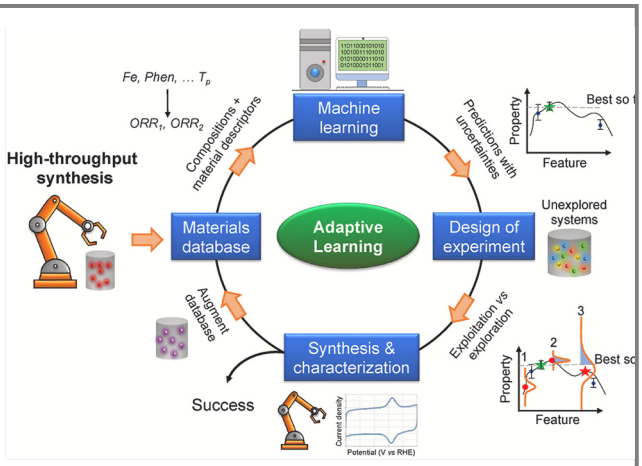


Figure. Developed and implemented adaptive learning design loop with uncertainty quantification to model and guide high-throughput synthesis of PGM-free catalysts.[5]

Relevance to MGI

As part of the DOE's Energy Materials Network (EMN), ElectroCat employs a systematic approach in which catalysts are synthesized and analyzed rapidly and comprehensively using high-throughput methods. These in turn are guided by computational modeling and machine learning, advanced characterization, and the fundamental electrocatalysis and materials knowledge housed across the national laboratory network. Streamlined data sharing with industry and academia partners is critical to the ElectroCat approach, rapidly building an understanding of PGM-free electrocatalysts across the field and, ultimately, enabling the incorporation of those materials into next-generation fuel cells and electrolyzers.

Technical Progress

Some key accomplishments that highlight the success of ElectroCat's systematic approach for PGM-free catalyst development include:

- *Identification of catalytic active sites:* Computational modeling using density functional theory and advanced characterization techniques such as in-situ X-ray absorption spectroscopy were used to understand catalytic active sites in Fe-N-C catalysts for the oxygen reduction reaction.[1,2]
- *Machine learning-directed synthesis of novel, high-performing catalysts:* High-throughput catalyst synthesis and performance correlations were investigated using several machine learning models. Output from the best model suggested "next-step" experiments that resulted in higher performing catalysts than were previously fabricated.[3,4,5]

- *Novel synthesis methods for improved catalyst activity:* Optimization of Ni-Fe composition coupled with novel, high surface area synthesis methods resulted in enhanced activity for the oxygen evolution reaction in alkaline electrolyte.[3]

Future Plans

ElectroCat is continuing to apply its data science-guided high-throughput synthesis methods specifically to Fe-N-C catalysts for the oxygen reduction reaction in fuel cells, pushing the boundaries of catalytic activity and stability, simultaneously. The consortium plans to implement best-in-class high-throughput-synthesized Fe-N-C catalysts in polymer electrolyte fuel cells (PEFCs) and continue expanding their work in low-temperature electrolyzer catalyst development for both oxygen and hydrogen evolution reactions.

Broader Impacts and Workforce Development

ElectroCat has already partnered with universities on the list of Minority Serving Institutions (MSIs) and plans to partner next year with Historically Black Colleges and Universities (HBCUs) on fuel cell and electrolyzer catalyst development projects. Students in selected projects will have an opportunity to work directly with the staff and post-docs at the core ElectroCat national laboratories. In addition, ElectroCat is committed to hiring and training new post-docs to conduct material synthesis, electrochemistry, and computational modeling work that is critical to the success of the consortium.

Data Management and Open Access

ElectroCat maintains a Data Hub where it stores data collected and models used. Industry and academic partners also share data through the Data Hub. Streamlined data sharing with these partners is critical to the ElectroCat approach, rapidly building an understanding of PGM-free electrocatalysts across the field and ultimately, enabling the incorporation of those materials into next-generation fuel cells and electrolyzers.

Advancing Along the Materials Development Continuum and Partnerships to Translation

By pooling their expertise, ElectroCat's national laboratory partners (co-led by Los Alamos National Laboratory and Argonne National Laboratory, with partners Oak Ridge National Laboratory and National Renewable Energy Laboratory) will advance the tools needed to model, synthesize, characterize, and optimize PGM-free catalysts and electrode structures to the point that they are easily applied to a broad range of catalyst systems and set a standard for rapid material analysis and development. The consortium approach allows for efficient collaboration between multiple lab partners and provides a structure for outside stakeholders to leverage the expertise at the core national labs to accelerate innovation. Such capabilities include material synthesis and processing, catalyst and electrode characterization, and computational material modeling.

Publications and References

A list of ElectroCat publications can be found at https://www.electrocat.org/electrocat-publications/

1. L. Osmieri, R. K. Ahluwalia, X. Wang, H. T. Chung, X. Yin, A. J. Kropf, J. Park, D. A. Cullen, K. L. More, P. Zelenay, D. J. Myers, K.C. Neyerlin, *Appl. Catal. B: Environ.*, 257, 117929-117941 (2019).
2. H. Yu, M. Zachman, D. Myers, R. Mukundan, H. Zhang, P. Zelenay, K. Neyerlin, and D. Cullen, *Microsc. Microanal*. 27, 974-976 (2021).
3. L. Osmieri, H. Yu, R. P. Hermann, M. E. Kreider, H. M. Meyer III, A. J. Kropf, J. H. Park, S. M. Alia, D. A. Cullen, D. J. Myers, P. Zelenay *Appl. Catal. B: Environ.*, 348, 123843 (2024).
4. M. Karim, M. Ferrandon, S. Medina, E. Sture, N. Kariuki, D.J. Myers, E.F. Holby, P. Zelenay, and T. Ahmed, *ACS Appl. Energy Mater.,* 3, 9083-9088 (2020).
5. W. J. M. Kort-Kamp, M. Ferrandon, X. Wang, J. H. Park, R. K. Malla, T. Ahmed, E. F. Holby, D. J. Myers, P. Zelenay, *J. Power Sources*, 559, 232583 (2023).

Comsuite: combining electronic with quantum embedding methods to predict the properties of correlated electron materials

Lead Investigator: Gabriel Kotliar, Kotliar@physics.rutgers.edu
Participating Institutions: Brookhaven National Laboratories, Rutgers University
Source of Support: DOE-BES
Website: https://www.bnl.gov/comscope/
Keywords: Software-development, correlated-electron-materials, theoretical-spectroscopy

Project Scope
The mission of Comscope, the Center for Theoretical Spectroscopy and Material Design, is to develop, validate and disseminate Comsuite, an open source, publicly licensed electronic structure package combining quantum embedding methods such as DMFT(Dynamical Mean Field Theory) and electronic structure functional and diagrammatic methods, to describe and predict the physical properties of strongly correlated electron materials.

Relevance to MGI
Strongly correlated electron materials are not well described by standard electronic structure methods based on density functional theory, and require new concepts, algorithms and software tools, which are an integral part of the materials genome initiative. Comsuite successfully treats both static and dynamic correlations which are ubiquitous in this class of systems.

Technical Progress
We achieved the first complete prototype of Comsuite suite of codes. It contains advanced electronic structure methods using density functional and diagrammatic methods, state of the art impurity solvers, quantum embedding modules (DMFT and RISB), postprocessing tools that allow use of theoretical spectroscopies and novel computer science tools to facilitate its use and development (Portobello) . Comsuite's most time consuming modules have also been designed to work in exascale machines.

Future Plans
We plan further integration of Comsuite codes and comparison of results achieved against available experiments, together with predictions for future experiments for further validation, in the spirit of the materials genome project.

Broader Impacts and Workforce Development
Many postdoctoral scientists who worked in Comscope have now been integrated into the workforce, both in industrial and academic positions.

Data Management and Open Access
Codes developed in this project are fully open source and public licensed. The algorithms and the codes developed by our project have both been published in peer reviewed journals, such as Computer Science Communication, thus ensuring its long-term availability to the community.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Strongly correlated electron materials, have unique functionalities and offer the path to qualitative improvements in existing technologies, as well as completely new technologies.

Modern implementations of the density functional theory approach and its extensions are an important foundation of both materials research and the MGI project. We hope that quantum embedding methods, coupled to all electron ab-initio electronic structure tools, including those developed by Comscope, will play a similar role in the future, thus opening new possibilities for material design, by employing strongly correlated electron materials.

Publications and References

1. Toward a predictive theory of correlated materials, PRC Kent, G Kotliar, Science 361 (6400), 348-354 (2018)
2. Linearized self-consistent quasiparticle GW method: Application to semiconductors and simple metals, AL Kutepov, VS Oudovenko, G Kotliar, Computer Physics Communications 219, 407-414 (2017)
3. Slave Boson Theory of Orbital Differentiation with Crystal Field Effects: Application to UO2, Nicola Lanatà, Yongxin Yao, Xiaoyu Deng, Vladimir Dobrosavljević, and Gabriel Kotliar, Phys. Rev. Lett. 118, 126401 (2017)
4. ComDMFT: a massively parallel computer package for the electronic structure of correlated-electron systems, S Choi, P Semon, B Kang, A Kutepov, G Kotliar
Computer Physics Communications 244, 277-294 (2019)
5. EDRIXS: An open source toolkit for simulating spectra of resonant inelastic x-ray scattering, YL Wang, G Fabbris, MPM Dean, G Kotliar, Computer Physics Communications 243, 151-165 (2019)
6. Self-consistent GW method: O (N) algorithm for polarizability and self energy
AL Kutepov, Computer Physics Communications 257, 107502 (2020)
7. Accelerated impurity solver for DMFT and its diagrammatic extensions, C Melnick, P Sémon, K Yu, N D'Imperio, AM Tremblay, G Kotliar, Computer Physics Communications 267, 108075, (2021)
8. Portobello-Quantum embedding in correlated materials made accessible, R Adler, C Melnick, G Kotliar, Computer Physics Communications 294, 108907 (2024)
9. ComDMFT v. 2.0: Fully self-consistent ab initio GW+ EDMFT for the electronic structure of correlated quantum materials, B Kang, P Semon, C Melnick, G Kotliar, S Choi
arXiv preprint arXiv:2310.04613 (2023)
10. Orbital-Selective Mott Transition Effects and Nontrivial Topology of Iron Chalcogenide, Minjae Kim, Sangkook Choi, Walber Hugo Brito, and Gabriel Kotliar, Phys. Rev. Lett. 132, 136504 (2024)

Design and Optimization of Granular Metamaterials using Artificial Evolution

Lead Investigator: Rebecca Kramer-Bottiglio, rebecca.kramer@yale.edu
Participating Institutions: Yale University, University of Vermont
Source of Support: NSF-DMREF
Website: https://www.eng.yale.edu/faboratory/
Keywords: Granular metamaterials, multifunctional materials, evolutionary algorithms, adaptive materials

Future metamaterials will exhibit increased dynamic plasticity, enabling responses to different environmental inputs or task demands by reconfiguring their physical structure. Granular metamaterials offer an advantageous platform for such dynamic programmability, as particle properties can be widely tuned to achieve different responses. Granular metamaterial response is dependent on many variables, including the grain arrangement, grain mass, modulus, and shape, friction or other interactions between grains, and boundary conditions of the granular assembly. With such a vast number of possible combinations of micro-structural variables, the task of designing the complex relationship between microstructure and bulk properties is daunting. We are applying evolutionary algorithms to efficiently search the immense parameter space for granular metamaterial designs with specific material properties, as well as identify how a design can be perturbed to push it from one set of desired bulk properties to another.

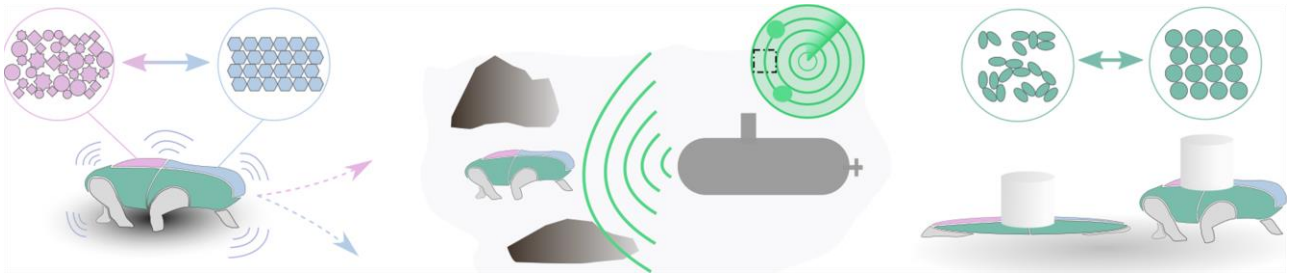


Figure 1. An example application for adaptable granular metamaterials. Materials with adaptable properties could enable a robot with (1) different responses to vibration, which could enable vibration-driven locomotion; (2) acoustic cloaking during covert missions; and (3) tunable bulk stiffness to adjust between compliance and load-bearing tasks.

Project Scope

Our effort seeks to establish a new artificial intelligence-driven approach to the design and optimization of granular metamaterials with adaptable properties. New knowledge and tools to be generated by this project include: (i) New evolutionary algorithms for granular metamaterials capable of editing their own configuration and properties; (ii) New discrete element method (DEM) simulations that can predict the properties of granular materials with active grains; and (iii) New synthesis strategies for multifunctional grains and grain assemblies.

Relevance to MGI

Our project aims to answer two questions: (1) How can we automatically design granular assemblies with specific desired material properties? (*i.e.*, What should the grains' arrangement, moduli, shapes, etc. be to yield a given bulk property?); and (2) How can we automatically design a series of granular assemblies that allow continuous, time-ordered changes in material properties? To answer these questions, we are developing a closed-loop procedure wherein physics-based discrete element simulations, evolution-based optimization, and physical realizations are combined to produce granular metamaterials with desired, optimal, and adaptable bulk properties.

Technical Progress

Our technical progress includes:

Adaptive force chains in granular metamaterials. Under an applied load, granular packings form force chain networks influenced by the contact network and grain stiffness. We investigated packings of variable stiffness

particles, directing force chains by changing individual particle stiffness on demand. Each particle consists of a silicone shell and a core of Field's metal, which melts and softens with an electric current through a copper heater. As it cools, the particle regains its original stiffness. Using an evolutionary algorithm and discrete element method simulation, we optimized the mechanical response of granular packings. Experiments with a 2D assembly of variable stiffness particles measured force outputs via photoelasticity. Our results represent a first step towards robotic granular metamaterials that can dynamically adapt their mechanical properties.

Polycomputation in granular metamaterials. One type of material property adaptation we are studying is computing capability. By applying input vibrations to a subset of grains in a granular assembly, we can interpret the measured output vibrations at another subset of grains as computational outputs. While previous research has shown that changing the input frequency to an assembly changes the output frequency, thereby altering the logic gate, we have demonstrated that this process can be inverted. By adjusting the stiffness of individual grains, we can design logic gates that adapt to the same input frequency. Additionally, we discovered that we can evolve granular materials capable of "polycomputing," where multiple inputs as vibrations at different frequencies produce multiple computational results, which can be detected as vibrations at different frequencies at the output grain.

Tessellated granular metamaterials. The shear modulus of granular packings typically increases with pressure due to frequent particle and contact network rearrangements. We are developing a class of granular metamaterials where the shear modulus can either increase or decrease with pressure without particle rearrangements. Using DEM simulations and experimental studies, we created "tessellated" granular metamaterials, which are divided into small compartments containing fewer than 10 grains each. Our simulations of tessellated parallelograms filled with soft disks show that the shear modulus can be precisely controlled—and notably designed to decrease with increasing pressure—without particle rearrangements. These findings present a novel methodology for designing granular materials with customizable pressure-dependent mechanical responses.

Cost of adaptation in granular metamaterials. Drawing parallels between adaptive shape-changing robots and adaptive property-changing materials, we are designing ``robograins" that can individually adapt their stiffness, size, and shape to collectively adapt a granular material's property state. Herein, we are studying the energetics of dynamic reconfiguration. Just as there exist infinite possible paths for a locomotion robot, there analogously exists infinite possible grain-level adaptations to achieve a desired time-ordered property state progression for a granular material. What is the most efficient adaptation path? Is it energetically favorable to wildly adapt one grain or to mildly adapt many grains, if both options will produce the same overall property state? This project is applying tools and strategies from robotics towards the design and control of adaptive materials, representing a conceptual shift with broad opportunities for impact.

Future Plans

We aim to enhance our particle capabilities, which currently include variable stiffness (gradients and binary switching) and variable size (particle growth and shrinkage), by incorporating variable shape. As we increase the number of free variables, we anticipate that the simulation environment, the multi-objective search algorithm, and the fabrication of the evolved designs will become increasingly complex.

Broader Impacts and Workforce Development

Our primary activity to broaden participation in the design of next-generation adaptable materials and robots will be the creation a website, Twitch Plays Soft Robotics, through which members of the public can collaborate to remotely "drive" a real soft robot. This new interactive Twitch channel will build upon the success of our team's prior introduction of Twitch Plays Robotics.

Data Management and Open Access

Digital outputs are publicly available through publications posted on the PIs' websites.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We expect the application of evolutionary algorithms to locally adaptable materials, such as granular assemblies, to enable increasingly sophisticated, programmable, and computationally dense metamaterials.

Publications

1. Witthaus, S., Parsa, A., Pashine, N., Zhang, J., Bongard, J., O'Hern, C., Kramer-Bottiglio, R., 2024. **Evolution of adaptive force chains in reconfigurable granular metamaterials**. Under review.
2. Beaulieu, S., Welch, P., Parsa, A., O'Hern, C., Kramer-Bottligio, R., & Bongard, J., 2024. **Refractive Computation: parallelizing logic gates across driving frequencies in a mechanical polycomputer**. To appear in the Proceedings of the 2024 *Artificial Life (ALife) Conference*.
3. Goyal, M., Lambo, M., Bongard, J. and Kramer-Bottiglio, R., 2024, April. **Merging Variable Stiffness Fiber Patterns on Multi-Shape Robotic Sheets**. In *2024 IEEE 7th International Conference on Soft Robotics (RoboSoft)* (pp. 894-899). IEEE.
4. Zhang, J., Wang, D., Jin, W., Xia, A., Pashine, N., Kramer-Bottiglio, R., Shattuck, M.D. and O'Hern, C.S., 2023. **Designing the pressure-dependent shear modulus using tessellated granular metamaterials**. *Physical Review E*, 108(3), p.034901.
5. Parsa, A., Witthaus, S., Pashine, N., O'Hern, C., Kramer-Bottiglio, R. and Bongard, J., 2023, July. **Universal Mechanical Polycomputation in Granular Matter**. In Proceedings of the *Genetic and Evolutionary Computation Conference* (pp. 193-201).
6. Pashine, N., Wang, D., Zhang, J., Patiballa, S.K., Witthaus, S., Shattuck, M.D., O'Hern, C.S. and Kramer-Bottiglio, R., 2023. **Tessellated granular metamaterials with tunable elastic moduli**. *Extreme Mechanics Letters*, 63, p.102055.
7. Bongard, J. and Levin, M., 2023. **There's plenty of room right here: Biological systems as evolved, overloaded, multi-scale machines**. *Biomimetics*, 8(1), p.110.
8. Pashine, N., Nasab, A.M. and Kramer-Bottiglio, R., 2023. **Reprogrammable allosteric metamaterials from disordered networks**. *Soft Matter*, 19(8), pp.1617-1623.
9. Parsa, A., Wang, D., O'Hern, C.S., Shattuck, M.D., Kramer-Bottiglio, R. and Bongard, J., 2022, July. **Evolving programmable computational metamaterials**. In Proceedings of the *Genetic and Evolutionary Computation Conference* (pp. 122-129).
10. Parsa, A., Wang, D., O'Hern, C.S., Shattuck, M.D., Kramer-Bottiglio, R. and Bongard, J., 2022, April**. Evolution of Acoustic Logic Gates in Granular Metamaterials**. In *International Conference on the Applications of Evolutionary Computation* (Part of EvoStar) (pp. 93-109). Cham: Springer International Publishing.

Accelerating the Design of Adhesives with Nanoscale Control of Thermomechanical Properties

Lead Investigator: Dan Krogstad, dkrogsta@illinois.edu
Participating Institutions: University of Illinois Urbana-Champaign (Illinois), University of Illinois Chicago (UIC), Purdue University, Air Force Research Laboratory
Source of Support: NSF-DMREF
Website: None
Keywords: Adhesives, Epoxy, Block Copolymers, Molecular Dynamics, Terahertz Time-Domain Spectroscopy

Project Scope

The primary objective is to develop a fundamental understanding of the multiscale structure-property relationships of high-toughness, hierarchical epoxy/block copolymer (BCP)/ionic liquid (IL) adhesives that will enable the rational design of next generation adhesives. Specifically, we will develop experimentally-validated multiscale models to increase our understanding of block copolymer self-assembly in epoxy, the origins of the adhesion forces, and other key mechanical properties (toughness, modulus) for hierarchically ordered adhesives. Model validation will be achieved through the use of a combination of in situ, multi-scale structural, chemical, rheological, and mechanical characterization methods. The results from the experiments and models will be integrated with machine learning (ML) tools to create a tool for adhesive property prediction and design.

Relevance to MGI

The factors that influence the structure and properties of these hierarchical epoxy adhesives are inherently multiscale. Therefore, it is critical to utilize experiments and models that can probe different length and time scales of these materials, and then link them together to obtain a detailed understanding of these complex systems. One of the earliest examples of our approach is in the development of models to predict the self-assembly of the BCPs in the ionic liquid/epoxy systems. In this instance, the molecular dynamics (MD) simulations that are being performed at UIC on the BCP self-assembly in ILs, are being performed at the same molecules as the validation experiments being performed at Illinois with the small angle x-ray scattering (SAXS). Once the models have been validated, the simulation and experimental results will serve as inputs into a ML model to predict the self-assembly of a broader range of block copolymers and solutions, which will greatly reduce the time and cost of the development cycles.

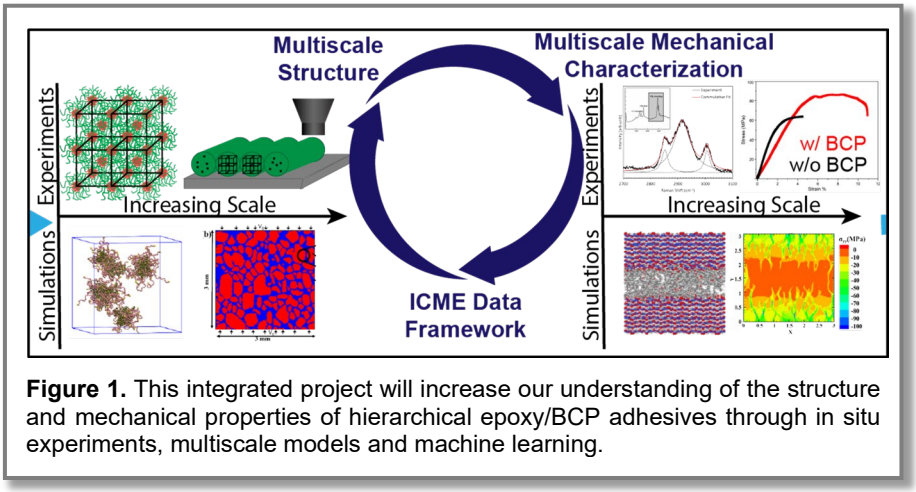


Figure 1. This integrated project will increase our understanding of the structure and mechanical properties of hierarchical epoxy/BCP adhesives through in situ experiments, multiscale models and machine learning.

Technical Progress

Key technical progress was made towards the rheological characterization of the formulations, mechanical characterization of the epoxies, and the simulation of the BCP self-assembly in the IL.

In this project, we identified a consistent procedure to reliably characterize the rheological properties of the formulations. Specifically, we demonstrated the importance of the preshear conditions in obtaining consistent yield stress values from transient creep testing. Using these procedures, we established strong correlations between the yield stress of the epoxy/BCP/IL materials and the structural organization of the BCPs. We also investigated the impact of mixing procedures on the material properties of epoxy matrix including the component mixing order, the mixing procedure (steps, speed, and time), and the effect of vacuum on the rheology. Our research has shown that the mixing order and the effect of vacuum during mixing highly influenced the rheological properties of the materials. These experiments will be used to train an ML model for optimization of the procedures.

For mechanical testing, the epoxy/BCP/IL materials were cured in pre-defined dogbone samples to determine their behavior in the quasi-static regime, including the determination of the strain rate sensitivity and failure of the

materials. Full-field strain measurements were obtained using digital image correlation (DIC). The quasi-static stress-strain behavior of the polymer composite was obtained at multiple cross-head speeds, corresponding to multiple strain rates. The epoxy/IL composites (without BCP) exhibited brittle behavior with a modulus of approximately 3 GPa. The strain to failure was observed to be very low, close to 3%. The fracture surface exhibited several pores, with large pores in close proximity initiating subcritical crack growth. Once the size of these cracks reached critical values, they propagated catastrophically, causing fast and brittle fracture. These baseline results indicate the potential benefit of BCPs to improve the toughness of the composites. Additionally, recently developed processing methods will help reduce the air in the materials, and will enable more reliable mechanical testing results.

MD has been used to predict the self-assembly of the BCP in IL. We modeled the IL using a coarse-grained (CG) framework using Martini 3.0 force field. First, the anion CG model was built using Martini beads, and the non-bonded parameter was further modified based on the interaction levels. For the validation of the parameters, we analyzed the bulk density and radial distribution function of the CG model and compared with all-atomistic simulation data. We modified a previously established model for BCP self-assembly in water and subjected to simulation with accurate coarse-grained representation of our IL instead of the water. The next steps will involve the optimization of the BCP-IL interaction strength in the models to replicate the experimental self-assembly results.

Future Plans

The project approach has been split into three thrusts: 1) Design the formulations for BCP self-assembly and tailor the meso- and macrostructure using processing, 2) Characterize the multiscale mechanical response, and 3) Develop the data framework to enable multiscale linkages. In Thrust 1, the experimental characterization will focus on understanding the hierarchical structure of the BCPs in the adhesive, through microscopy and SAXS. AAMD-informed CGMD simulations will be used to increase our understanding of BCP micelle formation and calculate the strengths of adhesion. In Thrust 2, we will perform mechanical testing on the composites to determine the strain rate sensitivity in the quasi-static regime with rich data production. Terahertz time-domain spectroscopy will be used to analyze sub-surface defects and pores in the material. The dynamic behavior of the composite will also be studied at higher rates using drop hammer tests and shock compression tests. In addition to experiments, a simulation framework is being developed to predict stress maps in given microstructures based on loading and loading rates. Thrust 3 will focus on the development of a data framework that will be used to connect the computational database with the experimental database (currently in development) and ML tools.

Broader Impacts and Workforce Development

The broader impacts of this project include broadening participation in engineering and training of graduate and undergraduate students. We have been working to identify and engage students from currently underrepresented populations to participate in this research, as well as in the teaching and public outreach events that stem from this work by leveraging existing diversity programs. The students on this project will not only advance their technical knowledge in their fields, but they will be exposed to a diverse set of modern tools by working in this integrated team environment, which will enable them to be successful for careers in academia or in industry. In the first year, funding from this project has been used to (at least partially) train ten students and post-doctoral researchers, 60% of which are from underrepresented minorities in STEM.

Data Management and Open Access

The development of data schema tools to archive and organize information is the first step towards integrating computational tools with experimental data that accelerate development. We have been working diligently to develop a data schema for the experimental data and metadata associated with epoxy formulation, processing methods, characterization methods, and materials properties. We are now building out a database based on these schemas. We are focusing on the development of a graph-based database, since a graphical schema can preserve material history and relationships, yet still allow for tabular outputs. The development of this database is critical to ensuring the experimental data follows FAIR data principles and will enable the integration of the experimental data with the existing computational databases and the machine learning tools.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The development of the adhesives data framework using FAIR data principles will ensure that the resulting information will be widely available and can be used to help accelerate the development of a wide variety of related advanced polymer systems. The collaboration with AFRL will help promote translation of these results into AFRL-relevant materials systems. The tools can also be used to accelerate the development of sustainable epoxy adhesives systems through the analysis of bio-sourced epoxy monomers with cellulosic nanocrystals.

Publications and References

There have been no submitted publications yet.

Accelerating Materials Discovery: Understanding Attitudes and Habit Regarding Data Use and Sharing

Lead Investigator: Lisa B. Lewis, lblewis@albion.edu
Participating Institutions: Albion College/Purdue University, Johns Hopkins
Source of Support: NSF Cross Cutting Activities Program
Website: none
Keywords: survey, culture, data sharing, data use

Project Scope

The Materials Genome Initiative has the goal of accelerating the pace of scientific discovery through the use of data sharing and data methodologies (e.g., machine learning). The extent to which the stakeholders in the materials research community have the knowledge and ability to embrace the habits and practices necessary relies upon a fundamental change in culture about how we think about the practice of science. With this in mind, we surveyed researchers with a goal of understanding the prevalence of and major impediments to data sharing as well as the prevalence of data-centric research methodologies.

Relevance to MGI

We surveyed researchers with a goal of answer these major research questions:

(1) How prevalent is the sharing and use of data in materials research?
(2) What are the current major impediments to FAIR data sharing?
(3) What are general attitudes with respect to the use of data in materials research? Are there differences based on field of expertise?
(4) How prevalent is the use of data-centric research approaches (such as machine learning and artificial intelligence) in materials research? Are there differences based on field of expertise?

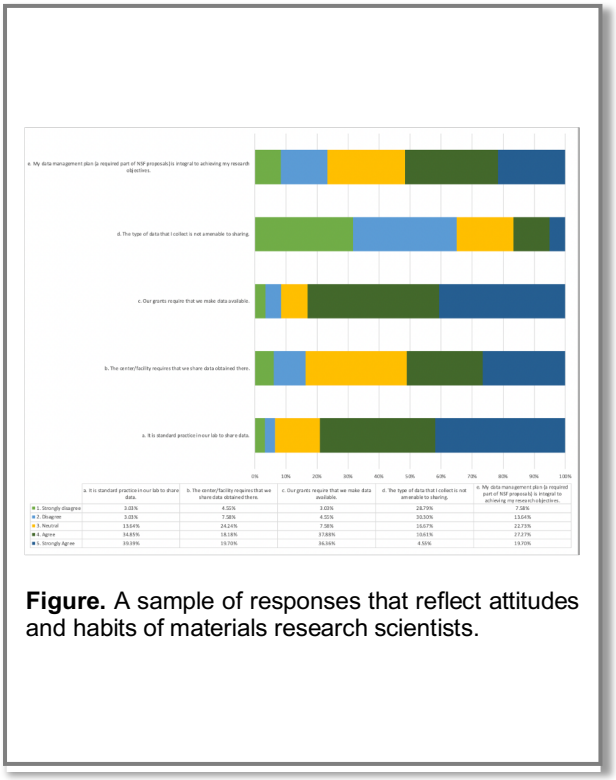


Figure. A sample of responses that reflect attitudes and habits of materials research scientists.

Technical Progress

More than eighty research scientists participated in our survey and a little over half of our participants report using data methodologies in their research. Generally, our participants believe that the sharing of data and data products is valuable and report sharing primarily with collaborators and others in the research lab. Most participants understand that research protocols need to be modified to support data-centric research; however, only half of the respondents believe that the NSF data management plan is integral to achieving research objectives. We will report additional outcomes of the survey, including some correlations between habits and attitudes of researchers.

Future Plans

As we look to publish this work, additional analysis, including inter-rater reliability will be performed. We plan look to identify additional correlations between opinions and attitudes and the habits of researchers. Because respondents share their perceptions of needs for the community, this work can be used to shape future policy, program, and infrastructure decisions to support the materials science community in achieving MGI goals.

Broader Impacts and Workforce Development

More than one-third of respondents report not using data methodologies such as machine learning. One-third said it was not related to their interests and 30.8% responded that they lacked the background and skillset. This suggests that workforce development and training for faculty is an important need for the materials research community.

Data Management and Open Access

Once analysis is complete, de-identified data will be made readily accessible to the community through a website and DOI.

Advancing Along the Materials Development Continuum and Partnerships to Translation

As one participant remarked, “I think it is still a ‘Wild West’ out there with respect to data. All of these efforts need to begin with a sustainability model…” The adoption of national standards with a national data board is appealing because standards make data trustworthy. Respondents would like to see more sharing of raw data and not just the results of successful experiments. There is a need for a centralized database(s) that are open to the public and equipped with educational protocols adaptable to undergraduate and graduate students. Datasets must be machine readable and attribution and credit for published datasets is a must.

Publications and References

This work has not been published but this reference has been helpful in thinking about how culture and policy affect the success of MGI.

American Geological Union (AGU) Position Statement on Data: www.agu.org/Share-and-Advocate/Share/Policymakers/Position-Statements/Position_Data.

DMREF: Collaborative Research: High-throughput Screening of Electrolytes for the Next-generation Rechargeable Batteries

Lead Investigator: Tao Li, tli4@niu.edu
Participating Institutions: University of Michigan, University of Illinois at Chicago
Source of Support: Enter NSF-DMREF
Website: none
Keywords: small angle X-ray scattering, electrolytes, high-throughput, molecular dynamics, machine learning

Project Scope

We hypothesize that the ionic environment and structural heterogeneity are crucial in defining the ion transport mechanism. Our proposed research aims to uncover the structure-property relationships of battery liquid electrolytes. We will systematically vary the composition and concentration of the electrolytes to determine the optimum solution for rechargeable batteries. Our approach integrates high-throughput experimental characterization, computational simulations, and data-driven analysis in a closed feedback loop. By leveraging the research team's expertise in high-throughput experiments (**Li**), simulations (**YZ and Ngo**), and data analysis, we aim to rationally design a new generation of liquid electrolytes and understand the fundamental interactions between ions and solvents.

Relevance to MGI

While the Materials Genome Initiative allows scientists to traverse large swaths of chemical space of electrolytes, high-throughput methods limit the development. Furthermore, the recent observation of larger nanoaggregates in electrolytes suggests that the previous understanding of electrolyte solvation structures should be revisited. The proposal focuses on building tools to readily link ab initio simulations with predictions of electrolyte macroscopic behavior by bridging our team's expertise, as shown in **Figure 1**. **Li** is an expert in high-throughput experimentation/characterization and has screened many electrolyte combinations for solvated structures with SAXS/WAXS. On the computational side, **Ngo** has extensive experience studying ion solvation structures and kinetics with MD, while **YZ** has expertise in applying machine learning methods to guide high-throughput computational screening as well as neutron scattering. Our approach will use advanced characterization techniques to measure solvation structures and bulk transport properties for a large number of chemical parameters while gaining molecular insights from computational methods such as AIMD and CMD. Machine learning methods will use results from high-throughput (HT) experimental platforms to make predictions to guide simulations, which will provide insights into narrowing the experimental parameter space. This approach will allow us to optimize electrolyte parameters for the next-generation electrolytes.

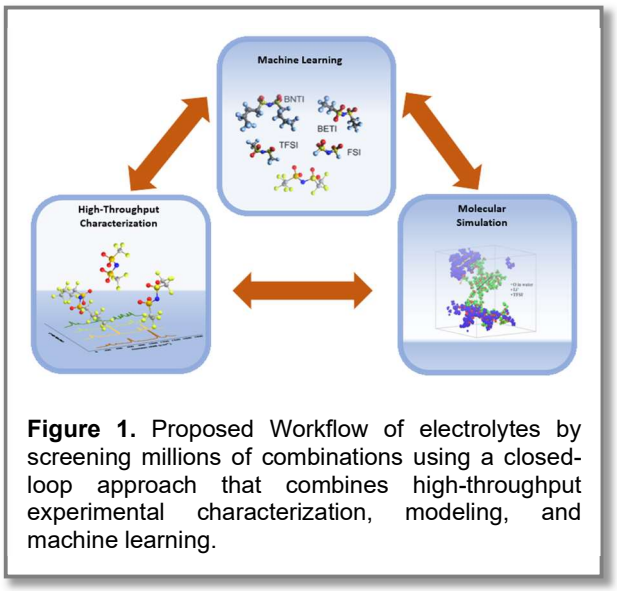


Figure 1. Proposed Workflow of electrolytes by screening millions of combinations using a closed-loop approach that combines high-throughput experimental characterization, modeling, and machine learning.

Technical Progress

SAXS experiment was carried out at 12ID-C of Advanced Photon Source (APS), and the in-situ Raman experiment was determined by using a Renishaw Raman spectroscopy at the center for nanoscale materials. **Figures 2** (a) and (b) show the SAXS and Raman profile. Combining the plots shows that the peak intensity centered at 1 $Å^{-1}$ decreases

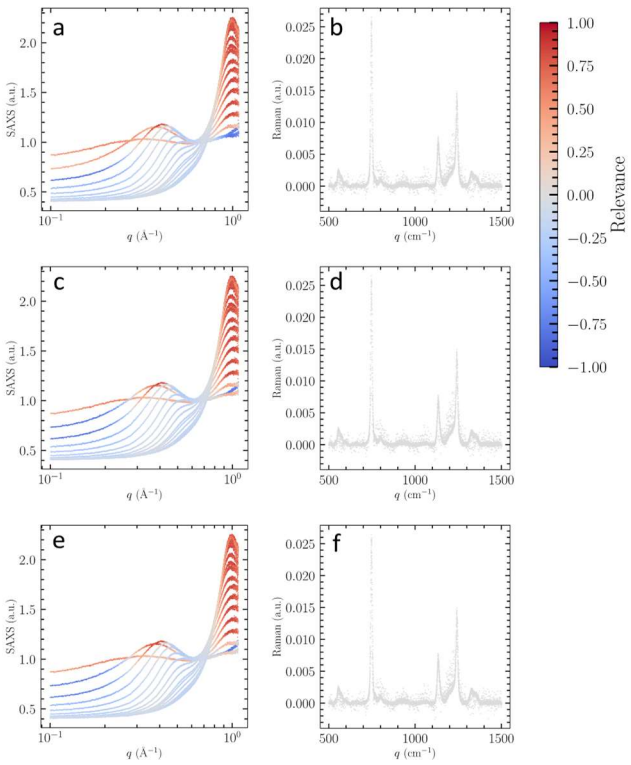


Figure 2. LRP explanations obtained for output neurons: (a~b) L_1, (c~d) L_2 and (e~f) L_3 from model B.

with more water injected into the system. Meanwhile, as the dilution proceeded, a new peak was formed and raised from around 0.4 $Å^{-1}$ and eventually moved to the low q region and decreased in intensity.

To provide explanations for how the HT SAXS and Raman data are mapped onto the low-dimensional space, we used Layer-Wise Relevance Propagation (LRP) to obtain such explanations. LRP is a framework that could analyze the prediction from a high-dimensional neural network. This framework outputs the relative importance (the relevance) of each input feature contributing to each latent variable on a particular sample. We took model B as an example and showed that the predictions of all three latent variables contributed much more from the SAXS data than Raman data (**Figure 2**), which suggests that the distribution of the samples on the low-dimensional representation depends more on the SAXS data than Raman data. The color represents the relevance of the data in the prediction.

Future Plans

High throughput characterization will be used to generate a large amount of data. Machine learning will be used to take advantage of the database for the training.

Broader Impacts and Workforce Development

A total of five graduates, three undergraduates, and one postdoc have been involved in this project.

Data Management and Open Access

The data has been shared by three PIs and stored in the box folders. For the published work, the data is also open to the public and could be obtained by contracting each PI.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The electrolyte could be discovered within a shorter time with our current work. Our results could accelerate the discovery of new electrolytes. One patent has been filed, and PI plans to commercialize the technology.

Publications and References

1. X. Liu, R. Winans, A. Ngo*, Tao Li*, *Exploring Solvation Structure for Rational Design of Advanced Electrolytes for Next Generation of Li-ion Battery*, Applied Physic Review, **11**, 021307 (2024). DOI: doi.org/10.1063/5.0187154
2. X. Lyu, H. Wang, X. Liu, L. He, C. Do, S. Seifert, R. Winans, L. Cheng*, Tao Li*, *Probing the Solvation Structure of Methanol-in-Salt Electrolyte*, ACS Nano, **18**, 7037-7045 (2024). DOI: doi.org/10.1021/acsnano.3c10469
3. X. Liu, L. Fang, X. Lyu, R. E. Winans, Tao Li.* *Unveiling the Liquid Electrolyte Solvation Structure by Small Angle X-ray Scattering*. Chemistry of Materials, **23**, 9821-9832 (2023) DOI: doi.org/10.1021/acs.chemmater.3c01648

Machine Learning Accelerated Design and Discovery of Rare-earth Phosphates as Next Generation Environmental Barrier Coatings

Jie Lian, Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, lianj@rpi.edu
Liping Huang, Materials Science & Engineering, Rensselaer Polytechnic Institute, huangl5@rpi.edu
Suvranu De, Mechanical, Aerospace & Nuclear Engineering, Rensselaer Polytechnic Institute, des@rpi.edu
Website: none
Keywords: Multicomponent rare-earth phosphate, environmental barrier coating (EBC), ceramic-matrix composite (CMC), steam oxidation and CMAS corrosion, microstructure design,

Project Scope

A data-driven approach based on experiments, computational modeling and machine learning is being developed to discover new rare-earth phosphates for environmental barrier coatings (EBCs). More than 30 single and multicomponent rare-earth phosphates have been synthesized and experimentally tested for performance under different conditions. The obtained experimental data is utilized to develop and improve computational models. For accelerated material design, element-based and microstructure-based machine learning (ML) models are being developed. These ML models guide the experimental design and accelerate the performance testing of EBCs. The data and models generated in the project are uploaded to the online repositories.

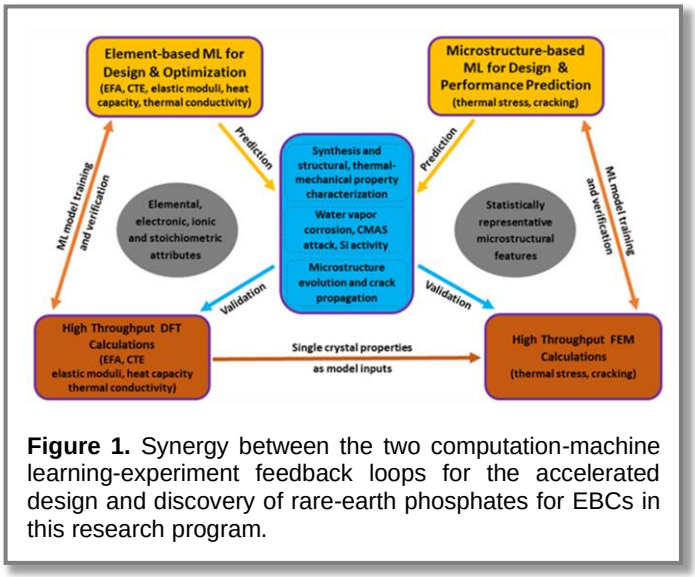


Figure 1. Synergy between the two computation-machine learning-experiment feedback loops for the accelerated design and discovery of rare-earth phosphates for EBCs in this research program.

Relevance to MGI

The data-driven approach developed in this project is based on a close collaboration between experiments, computational modeling and machine learning. Experimental synthesis and testing have been used to determine the thermomechanical properties of rare-earth phosphates as potential EBC materials and provide data for developing and validating computational models. These computational models assess the performance of EBC candidate materials and provide insights into their practical applicability under actual operating conditions. These insights are further used to provide feedback and recalibrate the design approach for improving material properties. Machine learning (ML) models are being developed using data from experimental measurements, microstructure maps and density functional theory (DFT) calculations. These ML models search the design space for suitable rare-earth phosphate compositions and microstructures with desired properties, which are then synthesized and tested in experiments. These iterative feedback loops among experiments, computation modeling, and ML modeling have increased our understanding of the performance of rare-earth phosphates for EBC applications. A fundamental knowledge base is being built through a material property database from experiments and DFT calculations. This database with computational and ML models is being used to accelerate the design of rare-earth phosphate for next-generation EBC applications.

Technical Progress

Single and multicomponent rare-earth phosphates (including Sc, Lu, Yb, Er, Y, Sm and Gd) with xenotime structures were synthesized and systematically characterized for phase stability, thermal expansion coefficients (CTE), thermal conductivity, and mechanical properties. These phosphates have CTE values close to that of SiC ceramic matrix composites (CMCs). Multicomponent phosphates exhibited lower thermal conductivity than single component phosphates, which is highly correlated with the cation size disorder. However, no clear trend was found for CTE values. This study also compared calcium-magnesium-alumina-silicate (CMAS) corrosion resistance of single and multicomponent phosphates at 1300 °C for different durations. Multicomponent phosphates show thinner reaction layer and better CMAS corrosion resistance than single component phosphates. Computationally, high throughput DFT calculations were carried out for entropy formation ability (EFA) and thermomechanical properties

of rare-earth phosphates using the AEL, AGL and QHA modules within the AFLOW framework. Multicomponent phosphates have a lower thermal conductivity and comparable CTE to single component phosphates, as validated by the experimental data. Element-based ML models based on graph neural networks and random forests have been developed to predict material properties such as formation energy, CTE and EFA. These ML models use data from online open-source databases (materials project and AFLOW) and data generated from DFT calculations in this project to make predictions. A second class of element-based ML models uses data from experiments, literature, and DFT calculations to identify the most significant elemental descriptors influencing CTE and EFA of multicomponent rare-earth phosphates. These ML models use linear regression and random forests to test different combinations of elemental descriptors that correlate with the CTE and EFA values and provide insights for experiments. The ML model based on experimental data revealed that elemental descriptors like ionic radius (RE element), size disorder (among multiple RE elements), mass disorder (among multiple RE elements) and electronegativity of RE elements most significantly influence the CTE of rare-earth phosphates.

Using experimentally obtained data, computational fracture models were developed to assess the fracture performance of different rare-earth phosphate materials under thermomechanical loads and CMAS corrosion. These models have also been used to study the effect of microstructure attributes (grain size, shape, and orientation) on the performance of rare-earth phosphates. These models showed that the fracture performance of rare-earth phosphate EBCs can be better than the 4th generation disilicate EBCs. A microstructure-based ML model is being developed to accelerate the performance prediction of EBC microstructures. The ML model uses the EBC microstructures to predict the fracture severity under thermomechanical load and CMAS corrosion, thus providing feedback on their performance.

Future Plans

We will continue developing integrated computational and experimental approaches based on ML-guided materials design to discover new rare-earth phosphates with optimized compositions and microstructures with enhanced performance as next-generation EBCs. In the upcoming year, we specifically plan to:
(1) Employ element-based ML models to identify potential multicomponent rare-earth phosphates for experimental synthesis and rapidly test their performance using microstructure-based ML models.
(2) Extend the computational models to predict the effect of water vapor corrosion on rare-earth phosphate EBCs.
(3) Carry out DFT calculations for thermomechanical properties of multicomponent rare earth phosphates.
(4) Synthesize multicomponent rare earth phosphates based on predictions from ML models and test their performance under CMAS and water vapor corrosion.

Broader Impacts and Workforce Development (250 words)

This program offers a unique opportunity for undergraduate and graduate students and young scientists to work in a dynamic and multidisciplinary environment. The project supported two postdoc research fellows and two PhD students, who are being educated and trained as the next-generation workforce skilled in the comprehensively integrated experiment-simulation-data analytics approach. In addition, five undergraduate students were trained during the last year and worked on different aspects of FEM modeling, machine learning, DFT calculations and experiments. The research team coordinated the Engineering Exploration Day at RPI to promote STEM among local communities in the Greater Capital Region of New York. One of the Co-PIs coached middle school and high school students to teach a group of elementary school students to do hands-on, interactive and fun STEM activities every Sunday afternoon. This helps high school and middle school students understand science concepts better by teaching others and getting younger students interested in pursuing STEM fields.

Data Management and Open Access (150 words)

The source codes for the computational models, high-throughput frameworks and machine learning models have been uploaded to the Github repository (link). The experimental data generated in this project is uploaded to the materials project database through the MPContribs portal in the online project (link).

Advancing Along the Materials Development Continuum and Partnerships to Translation

This project has the potential to transform the development of EBCs for CMCs by providing the knowledge base/design principles to optimize their structure and properties for reactive engine environments. The data-driven materials design approach will lead to the accelerated design and discovery of new materials with compositional complexity and configurational disorder. Our collaboration with industry, GE Global Research, will further enhance the technological relevance of our EBCs and speed up their incorporation into potential new applications.

Publications and References

1. Keith Bryce, Yueh-Ting Shih, Liping Huang, and Jie Lian. "Calcium-Magnesium-Aluminosilicate (CMAS) corrosion resistance of high entropy rare-earth phosphate ($Lu_{0.2}Yb_{0.2}Er_{0.2}Y_{0.2}Gd_{0.2})PO_4$: A novel environmental barrier coating candidate." *Journal of the European Ceramic Society* 43, no. 14 (2023): 6461-6472. https://doi.org/10.1016/j.jeurceramsoc.2023.06.030
2. Subrato Sarkar, Rahul, Bishnu P Majee, Keith Bryce, Lucy Zhang, Liping Huang, Jie Lian, and Suvranu De. "Fracture Characteristics of Rare-earth Phosphate under Molten Calcium-Magnesium Aluminosilicate Corrosion" Acta Materiala (Submitted)
3. Keith Bryce, Bishnu P Majee, Liping Huang, and Jie Lian, A systematic study of the thermomechanical properties and Calcium-Magnesium-Aluminosilicate (CMAS) corrosion of multicomponent rare-earth phosphates, Journal of Advanced Ceramics. (Submitted)
4. Bishnu P Majee, Keith Bryce, Liping Huang, and Jie Lian, Calcium–Magnesium–Alumina–Silicate (CMAS) corrosion resistance of LuPO4 at high-temperatures: As a potential environmental barrier coating, Journal of the European Ceramic Society (Submitted).

Symmetry-guided Machine Learning for the Discovery of Topological Phononic Materials

Lead Investigator: Bolin Liao, bliao@ucsb.edu
Participating Institutions: University of California Santa Barbara, Massachusetts Institute of Technology
Source of Support: NSF-DMREF
Website: https://dmref.org/projects/144
Keywords: topological materials, machine learning, phonon physics, thermal transport

Project Scope

The overarching goal of this project is to use a Materials Genome Approach to discover, simulate, synthesize and characterize novel materials hosting phonon modes with nontrivial topology. These topological phononic materials are ideal testbeds for emerging new physics in topological bosonic systems. Practically, nontrivial phonon topology can provide a new degree of freedom to control phonon scattering and to manipulate thermal and thermoelectric transport properties. We will develop machine-learning based methods to systematically identify topological phononic materials, synthesize and characterize them in a closed-loop fashion. Our study will establish the foundation for understanding the physical consequences of topological phononics states.

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Relevance to MGI

Our team will utilize a closed feedback loop approach to identify, simulate, synthesize and characterize novel topological phononic materials. We will first develop a machine-learning based method to accurately predict phonon properties of materials based on their crystal symmetry and chemical composition. For this purpose, we will also curate and establish a phonon property database for stoichiometric crystalline materials included in Materials Project. Machine learning predictions will be verified using first-principles phonon simulation and topological invariance analysis. Promising candidate materials will be synthesized as thin films and bulk single crystals and characterized using inelastic neutron and x-ray scattering, thermal transport, and surface-sensitive spectroscopy and scanning probe measurements. We will also incorporate machine-learning and data science methods to augment the sensitivity of the characterization methods. One recent example is shown in Figure 1, where a new machine learning framework based on matrix virtual notes (MVN) method is developed to be able to predict phonon frequencies of complex materials only with their crystal structure and chemical composition as inputs.

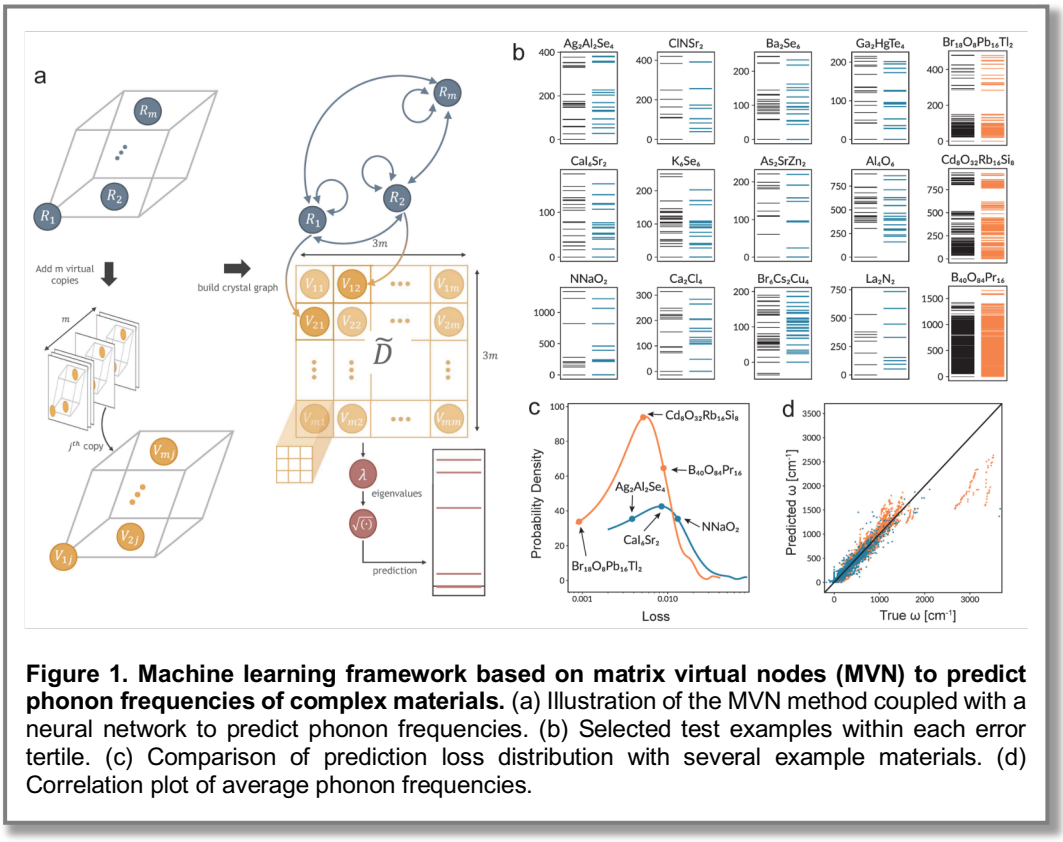


Figure 1. Machine learning framework based on matrix virtual nodes (MVN) to predict phonon frequencies of complex materials. (a) Illustration of the MVN method coupled with a neural network to predict phonon frequencies. (b) Selected test examples within each error tertile. (c) Comparison of prediction loss distribution with several example materials. (d) Correlation plot of average phonon frequencies.

Technical Progress

Building upon our progress in the previous period, where we demonstrated predicting the phonon density of states (DOS) with a variant of graph neural network (GNN), we continued developing new GNN methods to accurately and efficiently predict the full phonon dispersions as well as anharmonic properties in this period, which will serve as the basis for our planned high-throughput search for materials hosting topological phonon states. In our collaborative research effort (accepted in *Nature Computational Science*) by PIs Li and Liao, we introduced the Virtual Node Graph Neural Network (VGNN), a universally applicable methodology to extend GNN, differing from symmetry-augmented GNN by concentrating on managing output properties with variable or indefinite dimensions instead of minimizing the input data volume. We showcase the effectiveness of VGNN through the exploration of materials' phonon spectra and dispersion relations, highlighting its efficacy in addressing challenges related to high computational demands and restricted experimental resources (Figure 1). Our approach enables the assessment of phonon band structures directly from atomic structures in intricate materials, providing insights into group velocities, heat capacities, and density of states. These innovative structures hint at the potential evolution of flexible GNN design, allowing the use of intermediate pivotal quantities as essential learning parameters without mandating the insertion of target properties as output. This not only propels the advancement in material science by furnishing an efficient mechanism to compute phonon energies and structures but also fosters the optimization of phonon properties within an extensive structural design spectrum. In parallel, PIs Liao and Stemmer have worked on elucidating thermal and thermoelectric transport properties associated with topological surface states in quantum confined topological Dirac semimetals. In a recent joint publication in *Advanced Materials*, we systematically examined the magneto-thermoelectric transport properties of high-quality thin films of topological Dirac semimetal Cd_3As_2 and we discovered a significantly enhanced thermoelectric power factor in 25-nm thick quantum confined film. Through systematic transport and quantum oscillation measurements, we attributed the unusual thermoelectric properties to the topological surface states, providing a first example on enhanced thermoelectric performance via the topological surface states. These findings have significantly advanced our understanding of the impact of topology on thermal and thermoelectric transport properties in topological insulators and semimetals.

Future Plans

In the next Period, we plan to continue investigating the thermal transport properties in quantum-confined topological Dirac semimetal thin films, particularly aiming to examine the interaction between phonons, bulk Dirac electrons and the topological surface states. We will also examine thermal transport in chiral materials hosting Weyl phonon modes and their impact on thermal conductivity, especially its magnetic field dependence. We will also develop a Boltzmann transport theory for topological phonons including the impact of phononic Berry curvature.

Broader Impacts and Workforce Development

The project is currently supporting three graduate students, who will gain experience in both traditional material science and data science/machine learning. Liao has also hosted three summer undergraduate interns from underrepresented minority communities. Beyond workforce development, we have also developed and published an open-access phonon database and open-source software for phonon topology analysis. The PIs developed new courses and incorporated data science concepts into existing courses on material science.

Data Management and Open Access

The project has generated the following digital objects that are deposited onto online databases that are openly accessible to the public: (1) a machine-learning model for phonon properties; (2) a phonon property database; (3) a phonon topology analysis software and (4) educational course materials. All experimental and simulation data are properly annotated and published together with peer-reviewed journal articles. We identify the DOIs of the deposited data when the accompanying paper is published online.

Advancing Along the Materials Development Continuum and Partnerships to Translation

In this project, we aim to accelerate the development of materials with desirable thermal properties by incorporating machine-learning methods and high-throughput computation into thermal materials searching and modeling. We have established a phonon database that can significantly accelerate the development of materials with desirable thermal properties. Given the fundamental nature of the proposed project, we currently do not anticipation commercialization of the discovered topological materials in the near future.

Publications and References

1. N. Andrejevic, J. Andrejevic, B. Bernevig, N. Regnault, F. Han, G. Fabbris, T. Nguyen, N. Drucker, C. Rycroft and M. Li, *Machine-learning spectral indicators of topology*, Advanced Materials **34**, 2204113 (2022). DOI: 10.1002/adma.202204113
2. N. Andrejevic, Z. Chen, T. Nguyen, L. Fan, H. Heiberger, L. Zhou, Y. Zhao, C. Chang, A. Grutter and M. Li, *Elucidating proximity magnetism through polarized neutron reflectometry and machine learning*, Applied Physics Reviews **9**, 011421 (2022). DOI: 10.1063/5.0078814
3. T. Nguyen and M. Li, *Electronic properties of correlated Kagome metals AV_3Sb_5 (A=K, Rb, and Cs): A perspective*, Journal of Applied Physics **131**, 060901 (2022). DOI: 10.1063/5.0079593
4. K. P. So, M. Stapelberg, Y. Zhou, M. Li, M. Short and S. Yip, *Observation of dynamical transformation plasticity in metallic nanocomposites through a precompiled machine-learning algorithm*, Materials Research Letters **10**, 14 (2021). DOI: 10.1080/21663831.2021.2005700
5. N. Andrejevic, *Machine Learning-Augmented Spectroscopies for Intelligent Materials Design*, Springer Theses (2022). DOI: 10.1007/978-3-031-14808-8
6. Z. Chen, X. Shen, N. Andrejevic, T. Liu, D. Luo, T. Nguyen, N. Drucker, M. Kozina, Q. Song, C. Hua, G. Chen, X. Wang, J. Kong, and M. Li, *Panoramic mapping of phonon transport from ultrafast electron diffraction and machine learning*, Advanced Materials **35**, 2206997 (2023). DOI: 10.1002/adma.202206997
7. M. Mandal, N. Drucker, P. Siriviboon, T. Nguyen, A. Boonkird, T. Lamichhane, R. Okabe, A. Chotrattanapituk and M. Li, *Topological superconductors from a materials perspective*, Chemistry of Materials **35**, 6184 (2023). DOI: 10.1021/acs.chemmater.3c00713
8. W. K. Ouyang, A. C. Lygo, Y. B. Chen, H. Y. Zheng, D. Vu, B. L. Wooten, X. C. Liang, J. P. Heremans, S. Stemmer and B. L. Liao, *Extraordinary thermoelectric properties of topological surface states in quantum-confined Cd_3As_2 thin films*, Advanced Materials, 2311644 (2024). DOI: 10.1002/adma.202311644
9. M. Cheng, R. Okabe, A. Chotrattanapituk, M. Li, *Machine learning detection of Majorana zero modes from zero-bias peak measurements*, Matter **7**, 2507 (2024). DOI: 10.1016/j.matt.2024.05.028
10. R. Okabe, A. Chotrattanapituk, A. Boonkird, N. Andrejevic, X. Fu, T. Smidt, T. Jaakkola, Q. Song, T. Nguyen, N. Drucker, S. Mu, B. L. Liao, Y. Cheng and M. Li, *Virtual node graph neural network for full phonon prediction*, Nature Computational Science, in press (2024).
11. N. Drucker, T. Nguyen, F. Han, P. Siriviboon, X. Luo, N. Andrejevic, Z. Zhu, G. Bednik, Q. Nguyen, Z. Chen, L. Nguyen, T. Liu, T. Williams, M. Stone, A. Kolesnikov, S. Chi, J. Fernandez-Baca, C. Nelson, A. Alatas, T. Hogan, A. Puretzky, S. Huang, Y. Yu and M. Li, *Topology stabilized fluctuations in a magnetic nodel semimetal*, Nature Communications **14**, 5182 (2023). DOI: 10.1038/s41467-023-40765-1
12. S. Kajale, T. Nguyen, N. Hung, M. Li and D. Sarkar, *Field-free deterministic and non-volatile switching of all-van der Waals spin-orbit torque system above room temperature*, Science Advances **10**, eadk8669 (2024). DOI: 10.1126/sciadv.adk8669
13. M. Mandal, A. Chotrattanapituk, K. Woller, L. Wu, H. Xu, N. Hung, N. Mao, R. Okabe, A. Boonkird, T. Nguyen, N. Drucker, X. Chen, T. Momiki, J. Li, J. Kong, Y. Zhu, and M. Li, *Precise Fermi-level engineering in a topological Weyl semimetal via fast ion implantation*, Applied Physics Review **11**, 021429 (2024). DOI: 10.1063/5.0181361
14. Y. B. Chen, R. Y. Jin, B. L. Liao and S. Mu, Thermoelectric transport in Weyl semimetal $BaMnSb_2$: a first-principles study, Physical Review Materials, in revision (2024). arXiv: 2403.00997
15. N. Drucker, T. Nguyen, M. Mandal, P. Siriviboon, Y. Quan, A. Boonkird, R. Okabe, F. Li, K. Buragge, F. Funuma, M. Matsuda, D. Abernathy, T. Williams, S. Chi, F. Ye, C. Nelson, B. Liao, P. Volkov, and M. Li, Incipient nematicity from electron flat bands in a Kagome metal, submitted (2024). arXiv: 2401.17141

Collaborative Research: DMREF: Machine Learning-aided Discovery of Synthesizable, Active and Stable Heterogeneous Catalysts

Lead Investigator: Suljo Linic, linic@umich.edu
Participating Institution: University of Michigan – Ann Arbor
Website: https://alloy-synthesis.che.engin.umich.edu/
Keywords: Machine learning; heterogeneous catalysis; alloys

Project Scope

The objective of our DMREF project is to bring together a team of experts in machine learning (ML), computational catalysis, and catalytic experimentation to augment the current computational paradigm for catalyst discovery by creating a fundamental framework that will use not only descriptors of catalytic activity but also the descriptors of materials synthesizability and stability under reaction conditions. Specifically, we will develop a workflow for predicting the synthesizability, activity and stability of different catalysts, especially bimetallic alloys. We will focus on CO oxidation kinetics over bimetallic catalysts. We will use in-situ CO - Diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) to interrogate the sites responsible for CO adsorption on these bimetallic catalysts and how they vary as a function of temperature. We describe our approach in **Figure 1**. Success will be measured by the ability of the

Relevance to MGI

Our proposed work addresses two NSF's *Big Ideas*, namely: (1) "Harnessing the Data Revolution" by combining ML and data analytics with computational and experimental catalysis research, and (2) "Grow Convergent Research" by addressing major challenges at the interface of the energy and material science by designing catalysts that enable sustainable chemical transformations. In line with DMREF's goals, our work will: (1) closely couple computation, theory, and experimentation in our catalytic materials design strategies, (2) help lead a paradigm shift in the way catalysis researchers perform research through an integrated ML-aided approach, (3) make all of our data and developed ML algorithms available to the broader community via dissemination in public repositories and GitHub, and (4) create a Data Science for Catalysis Training Program to educate and inspire the next generation of the catalytic materials workforce. Ultimately, by moving ML for catalysis beyond the studies of highly idealized systems and by incorporating the impact of stability and synthesizability into our analysis, we hope to serve as a go-to entity for practitioners of catalysis who seek user-friendly inputs from first principles calculations.

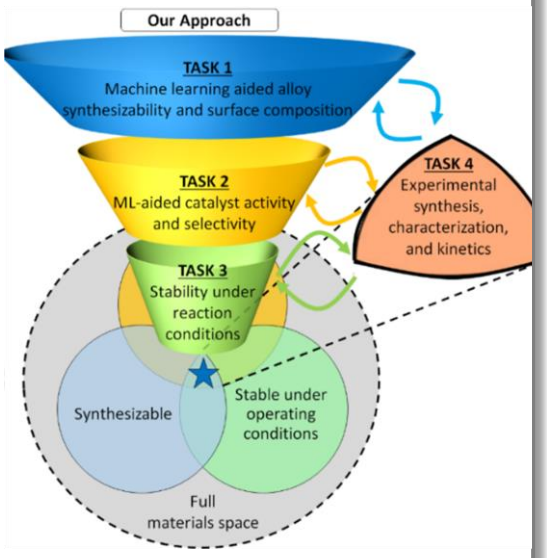


Figure 1. Our approach will consider synthesizability, surface composition of materials, activity (selectivity) and stability under operating conditions. This approach will yield a smaller phase space of potential target catalysts. Specifically, bimetallic alloys will be computationally screened based on synthesizability descriptors (TASK 1). The resulting stable alloy surfaces will subsequently be screened for the activity (selectivity) based on the activity (selectivity) descriptors using ML-aided DFT calculations (TASK 2). Finally, the top catalysts will be screened for stability under reactions conditions using ML-aided *ab initio* thermodynamics (TASK 3). Concurrent with the computational workflow, these catalysts will be synthesized and tested for catalytic performance and characterized under reaction conditions (TASK 4).

Technical Progress

Synthesis: Successfully synthesis of a library of alloys [PtM/support (M = Cu, Ru and Co); support = SiO_2] has been achieved using two synthesis methods: borohydride reduction and strong electrostatic adsorption. Monometallic catalysts have been also synthesized as benchmarks. The reproducibility of the synthesis protocols has been validated.

Characterization: The synthesized alloys were rigorously characterized by using x-ray diffraction, in situ CO-DRIFTS, X-ray absorption spectroscopy (XAS) and transmission electron microscopy with elemental mapping.

Kinetics studies: The alloys were used as catalysts for CO oxidation reaction in a packed-bed flow reactor. The kinetics of

the reaction catalyzed by different alloys was studied under steady-state conditions and the activation energies were extracted. It is found that the activation energies change with temperature, which is ascribed to the restructuring of the alloys. CO DRIFTS studies are used to offer mechanistic insights.

Database construction: Experimental synthesis procedures and all characterization data are being uploaded to our Metal Alloy Synthesis & Characterization Database (MASCD), which will serve as a public repository for metal alloy catalyst data. Currently we have several dozen materials synthesized and characterized. Graph-based procedures are generated and stored in MASCD, accessible through a progress web app (https://alloy-synthesis.che.engin.umich.edu/). Alloy characterization data are available for download and visualization. We will leverage MASCD to construct a computer-aided workflow and open-source tools for predicting the synthesizability, activity, and stability of catalysts.

Machine learning for materials studies: We identified high-performance iridium–molybdenum oxide electrocatalysts for water oxidation in acid using machine learning, Bayesian optimization, and experimental testing.[1] We are currently predicting the stability of numerous metal and alloy nanoparticle compositions on different metal oxides using neural network potentials as well as using interpretable machine learning to identify structure-property relationships.[2]

Future Plans

The future plans involve the expansion of the compositional space of the alloys to obtain the necessary volume of data to train ML algorithms in predicting the synthesizability of these catalysts. We will test these alloys for their CO oxidation kinetics and analyze them via spectroscopy under reaction conditions. In the future we plan to create a Data Science for Catalysis Training Program, where undergraduates from WSU come to U-M during the summer to learn the basics of data science and catalysis.

Broader Impacts and Workforce Development

Our goal is to train and equip the next generation workforce in material science and catalysis as well as to educate the general public. Our outreach efforts focus on student professional development, broadening science participation, and informal science communication to help create a world-class scientific workforce. Thus far, we have been organizing cross-disciplinary training for graduate and undergraduate students at the University of Michigan (U-M), providing them with a foundation to continue making scientific advances throughout their careers. For example, students funded by DMREF have received training on various characterization techniques for synthesis of alloys and running experiments. PhD students have visited Stanford Linear Accelerator and Argonne National Lab's Advanced Photon Source to learn about x-ray absorption spectroscopy (XAS). We also are contributing to the scientific community by constructing an open-source database (publicly available repository) that will be accessible by the community to guide the synthesis and characterization of heterogeneous alloy catalysts using various techniques. This characterization data will be accessible as a training tool for new researchers.

Data Management and Open Access

We are in the process of constructing a public database for all the alloy synthesis information and characterization data. This data is being loaded onto a searchable website where particular catalysts can be selected and their synthesis procedure and all the available characterization data can be displayed and downloaded. In addition, we plan to make available validated results of electronic structure calculations via public repositories (e.g., Novel Materials Discovery Laboratory and Materials Project). This type of dissemination may occur after, before, or instead of publication in a scientific journal. Also, all high-fidelity experimental catalysis data for CO oxidation will also be stored in the MASCD database and will be made available to the public.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We are pursuing several avenues to accelerate catalysis discovery and development. The first is to increase the reproducibility of synthesis and availability of synthesis information through the creation of the MASCD database, which will avoid redundancies in material synthesis efforts, and is designed to accelerate the process of new researchers synthesizing desired materials. The second avenue is in using ML to predict new materials, with a much lower cost than experimentally synthesizing materials. The third avenue is in developing techniques to accelerate or automate materials synthesis to increase the throughput and reproducibility of materials discovery.

Publications and References

1. J. A. Esterhuizen, A. Mathur, B. R. Goldsmith, S. Linic, “High-Performance Iridium–Molybdenum Oxide Electrocatalysts for Water Oxidation in Acid: Bayesian Optimization Discovery and Experimental Testing”, *Journal of the American Chemical Society* 146, 5511-5522 (2024).
2. J. A. Esterhuizen, B. R. Goldsmith, S. Linic, “Interpretable machine learning for knowledge generation in heterogeneous catalysis”, *Nature Catalysis* 5, 175-184 (2022).
3. J. Akinola, I. Barth, B. R. Goldsmith. N. Singh, “Electrocatalytic hydrogenation of phenol on platinum-cobalt alloys”, *Journal of Catalysis* 430, 115331 (2024).

Accelerating the Design and Development of Engineered Photonic Materials based on a Data-Driven Deep Learning Approach

Lead Investigator: Yongmin Liu, y.liu@northeastern.edu
Participating Institutions: Northeastern University, Purdue University, Georgia Institute of Technology
Source of Support: NSF-DMREF
Website: none
Keywords: engineered materials, photonics, metamaterials, deep learning

Project Scope

The overarching goal of this NSF DMREF project is to create a data-centric deep learning strategy that consolidates the properties of novel, tailorable constituent materials and their underlying symmetries and topology, to advance photonic metamaterials with user-defined spatial, spectral, linear, nonlinear, and quantum responses. The deep learning frameworks will enable the exploration of a vast parametric space with high efficiency to identify optimal metamaterial structures with desired properties. The research outcomes are expected to shed new light on the inter-dependent relationship among the structure, property, performance and processing of photonic materials across nano-, micro- and macro-scales.

Relevance to MGI

In accordance with the essence of MGI, this project aims to accelerate the pace of the discovery, design, and implementation of new engineered photonic materials, particularly photonic metamaterials, with prescribed properties through a data-driven strategy. We will create a comprehensive library of artificial meta-atoms and meta-molecules with arbitrary and complex shapes. We will then construct two-dimensional and three-dimensional metamaterials by engineering the constituent materials, geometric/topological degrees of freedom, amount of distinct unit cells and number of layers, with a speed that is orders of magnitude faster than conventional numerical simulation and optimization. This process will be based on the expertise of the team in photonic and topological metamaterial design combined with innovative deep learning algorithms and models, such as convolutional neural networks, transfer learning, physics-informed learning, and interpretable learning. Our research effort will start with theoretical analysis, numerical simulations, and deep learning model construction and training, followed by structure/material optimization, sample preparation, comprehensive characterization, and utilization of the engineered photonic materials for diverse applications. The research program will be developed in a bi-directional and closed-loop fashion. The results from fabrication, characterization and application will be fed back into theory and modeling to further advance the design and implementation of photonic materials.

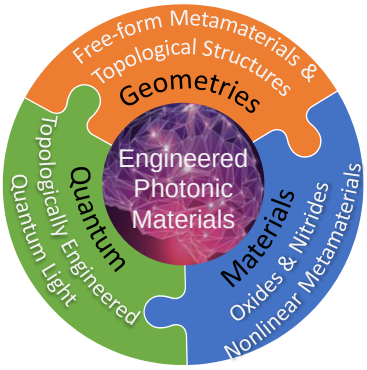


Figure 1. Illustration of the project, which aims to predict, design and implement engineered photonic materials by studying the geometry, material and quantum signatures based on a data-driven deep learning approach.

Technical Progress

We do not have progress to report, since the project has not officially started.

Future Plans

Figure 1 schematically illustrates the theme of the project. It consists of three research thrusts, including (1) establishing deep learning frameworks to construct photonic metamaterials with high efficiency and accuracy; (2) integrating information on the tailorable and nonlinear optical properties of the constituent material platform into deep learning models, to benefit the design and development of reconfigurable metamaterials; and (3) investigating

hybrid material systems that couple topological photonic structures designed by deep learning with quantum emitters and optical nonlinearities. The team will accomplish the interdisciplinary research by fusing theory, computation, deep learning, materials engineering, fabrication and experimentation in a closed-loop manner. This project will use advanced artificial intelligence techniques to develop new artificial photonic materials that can be engineered to have prescribed properties and surpass naturally occurring materials, and eventually drive transformative applications of photonic metamaterials for classical and quantum information processing.

Broader Impacts and Workforce Development

Integrating with the research work, the team will develop a comprehensive strategy aiming to foster students, especially those from underrepresented and minority groups, to become the leaders of future MGI and STEM workforce. The team will continue their dedicated efforts to K-12 education through diverse outreach programs at Northeastern University, Purdue University and GT, and Georgia Institute of Technology. We will enhance the undergraduate and graduate student experience through building new course materials, student mentorship and laboratory research. We will continue our efforts to strengthen the preparation, increase the participation, and ensure the contributions of individuals from the underrepresented groups by working with the relevant institutional programs. Furthermore, we will continue to engage cooperative education partner firms and collaborators for students to learn real-world applications.

Data Management and Open Access

To maximally advance the understanding and impact of the proposed work, the team will make every effort to make data in digital form that is Findable, Accessible, Interoperable and Reusable (FAIR). Besides the group websites of individual investigators, we plan to develop a website hosted at Northeastern University for this DMREF project to inform interested parties of the general scope, thematic progress, and specific results in a timely fashion. Simulation codes, deep learning models and training data, as well as experimentally characterized material properties will be made accessible to the public, following publication of the related research. For the purpose of data re-use and re-distribution, we will specify the metadata, that is, the means by which it was generated, detailed analytical and procedural information required to reproduce experimental results, and other pertinent information on the websites or in the journal publications.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Compared with conventional approaches that rely on numerical simulations and optimization algorithms, deep learning can simultaneously solve problems of forward prediction (i.e., output the optical responses when geometric parameters are given) and inverse design (i.e., identify the optimal structures based on the desired optical responses or functions) in less than seconds. Moreover, given the data-driven nature of deep learning, the model capacity can be substantially strengthened in use as we add more information into the database. This project will empower deep learning with new degrees of freedom, such as the constituent material properties, symmetries, topology and nonlinearity. By establishing this paradigm, we will be able to realize novel photonic structures and applications, including multi-dimensional meta-holograms showing distinct images at different wavelengths, broadband topological photonic crystals for robust slow light transport immune to disorder, and enhanced nonlinear metamaterials for quantum light generation.

Publications and References

We do not have publications to report, since the project has not officially started.

Elastomers Filled with Electro/Magneto-Active Fluid Inclusions: A New Paradigm for Soft Active Materials

Lead Investigators: Oscar Lopez-Pamies, pamies@illinois.edu; Zoubeida Ounaies, zxo100@psu.edu
Participating Institutions: University of Illinois Urbana-Champaign and The Pennsylvania State University
Website: https://publish.illinois.edu/liquidinclusions/team/
Keywords: Elastomers; Surface tension; Homogenization; Elasto-capillarity; Cloaking.

Project Scope

Elastomers filled with *fluid* inclusions — in contrast to conventional *solid* fillers — have emerged over the past few years as a new class of materials with the potential to revolutionize a wide range of technologies. Such properties stem, in part, from the very large deformations that the underlying liquid inclusions are capable of undergoing. In this context, the main objectives of this research are to: **i)** derive and numerically implement the homogenized equations describing from the bottom up the macroscopic electro/magneto-mechanical response of elastomers filled with fluid inclusions, **ii)** deploy the derived equations to guide the design of elastomers filled with liquid, liquid-metal and ferrofluid inclusions with optimized macroscopic electro- and magneto-mechanical properties, and **iii)** experimentally fabricate and test prototypes of such new materials.

Relevance to MGI

The interaction between theory, computation, synthesis, and characterization has proved critical for the success of this project thus far. As an example, simulations of the mechanical response of suspensions of monodisperse liquid inclusions provided bounds on how small the inclusions ought to be and how soft the elastomer ought to be in order for macroscopic behaviors to be dominated by the mechanics of the elastomer/liquid-inclusions interfaces. These bounds affected the protocol by which the materials were fabricated. On the other hand, the characterization of the mechanical response of the fabricated elastomers provided the means to identify via comparison with the theory how the surface tension of the elastomer/liquid interfaces depends on deformation.

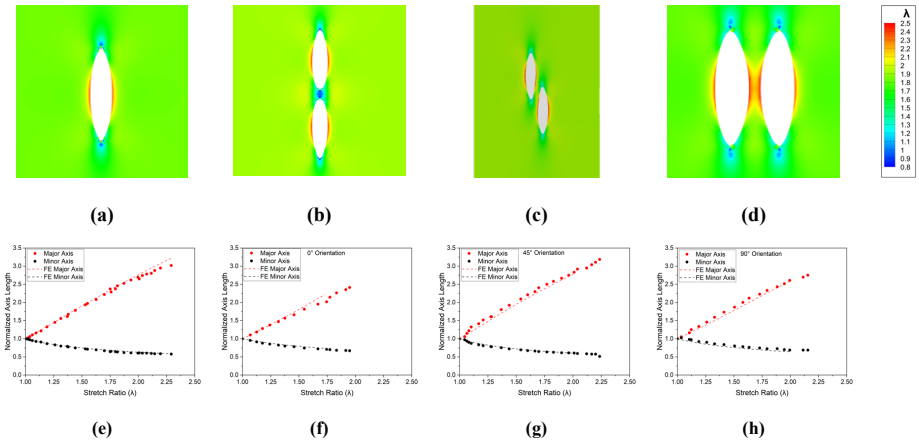
Technical Progress

Our broad goal is to advance the understanding of the mechanics of this emerging class of materials, namely soft polymers that are filled with liquid inclusions. Accordingly, we have completed a combined experimental/ theoretical study of the nonlinear elastic deformation of initially spherical liquid inclusions embedded in elastomers that are subjected to quasistatic mechanical loads. The existing literature *qualitatively* discusses that the addition of liquid inclusions to elastomers increases the overall deformability. This is in contrast to the addition of conventional fillers, which, being typically made of stiff solids, decreases the overall composite material deformability. There is also mention in the literature that the behavior of the interfaces separating a solid elastomer from embedded liquid inclusions results in a unique mechanical/physical response, one that, while negligible when the inclusions are "large", may dominate the macroscopic properties of the material when the inclusions are sufficiently "small". In contrast to this well-established *qualitative* understanding, the *quantitative* understanding of the mechanics and physics of elastomers filled with liquid inclusions is yet to be fully developed, which has been the focus of this project.

We made progress on two fundamental problems, both within the limit regime of negligible elasto-capillarity effects: **(i)** the problem of an isolated inclusion and **(ii)** that of a pair of closely interacting inclusions. The mechanics of deformation of liquid glycerol inclusions embedded in a PDMS elastomeric matrix were investigated in the large deformation regime. Experiments and simulations focused on the deformation of isolated individual inclusions and pairs of interacting inclusions under various loading configurations subjected to a range of 3D local stress fields. We fabricated polydimethylsiloxane (PDMS) elastomers filled with liquid glycerol inclusions. Using these specimens, we imaged either isolated or pairs of initially spherical liquid glycerol inclusions, and subjected them to macroscale uniaxial tension. For the specimens with pairs of inclusions, three orientations of the two inclusions with respect to the direction of the applied macroscopic tensile load were considered, 0˚, 45˚, and 90˚. The liquid glycerol was stained with a fluorescent dye that allows measuring the local deformation of the inclusions in situ via confocal scanning laser fluorescent microscopy. Theoretically, we used our recently developed framework wherein the elastomer is considered to be a nonlinear elastic solid, the liquid making up the inclusions is considered to be a nonlinear elastic fluid, and the interfaces separating the elastomer from the liquid inclusions can feature their own nonlinear elastic behavior (e.g., surface tension); we utilized this framework to carry out full-field simulations of the experiments. Our results show that the deformation of liquid inclusions is significantly non-uniform and strongly influenced by the presence of other liquid inclusions around them. Interestingly, they also show that the large compressive stretches

that localize at the poles of the inclusions may result in the development of creases.

The local stretch of individual inclusions was found to be repeatable, fully reversible and non-hysteretic. The stretch of the inclusions was only a function of the applied load and was independent of the inclusion size (70-500 μm), which is in agreement with deductions from Eshelby's theory. For the given matrix stiffness, surface tension effects would begin playing a role for liquid inclusions with diameters of the order of 20 - 100 nm. The experiments revealed a local and fully reversible mechanical instability emerging due to matrix compression at the poles of the inclusions at macroscopic and local stretch ratios of λ=1.7 and λ=0.7, respectively. The deformation of two interacting inclusions of similar dimensions that were in close proximity was axisymmetric about the axis connecting the inclusions' centers, however, mutual strain shielding resulted in deformation asymmetry for each inclusion. The computational framework, calibrated for the matrix behavior, provided very good predictions of the inclusion deformation (see figure) and was also able to predict the aforementioned instabilities.



FEM contour maps of local maximum principal stretch for **(a)** a single isolated inclusion, and for interacting inclusions under **(b)** 0°, **(c)** 45°, and **(d)** 90°loading configurations. The far-field stretch for all plots is λ=2. Experimental (markers) vs. computational (lines) deformation of **(e)** a single isolated inclusion, and pairs of interacting inclusions under **(f)** 0°, **(g)** 45° and **(h)** 90° loading configurations.

Future Plans

In this last year of the project (NCE), we are extending our investigation to the coupling between mechanical and magnetic properties of elastomers filled with ferrofluid inclusions. In particular, we are focusing on fabricating them in a variety of dimensions and volume content; results will be used to validate our modeling. We will also conduct the planned experiments with coupled fields, which will link up with the modeling effort and lead to further joint publications.

Broader Impacts and Workforce Development

This project is training three PhD students for careers in industry and/or academia. This training is truly unique as our biweekly Zoom meetings and written exchanges provide all three students with complementary perspectives (mathematics, mechanics, computation, and experimental materials science) in the design of an advanced class of materials.

Data Management and Open Access

We are finalizing our website for the project, where we will make accessible all the experimental data, codes, and publications that will be created. All our journal publications and 2 FE codes that have resulted from the project so far are also available from PI Pamies webpage and in GitHub. Moreover, we have publicized major outcomes from project through news outlets, see, e.g., https://cee.illinois.edu/news/researchers- derive-new-theory-behavior-new-class-materials.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Nothing to report yet.

Publications and References

1. K. Ghosh, V. Lefèvre, O. Lopez-Pamies, *Homogenization of elastomers filled with liquid inclusions: The small- deformation limit*. SIAM Journal of Applied Mathematics. Under review (2022)
2. Ghosh, K., Lopez-Pamies, O. 2022. *Elastomers filled with liquid inclusions: Theory, numerical implementation, and some basic results*. Journal of the Mechanics and Physics of Solids **166**, 104930 (2022).
3. V. Lefèvre, O. Lopez-Pamies, *The effective shear modulus of a random isotropic suspension of monodisperse rigid n-spheres: From the dilute limit to the percolation threshold*. Extreme Mechanics Letters **55**, 101818 (2022).
4. V. Lefèvre, G.A. Francfort, O. Lopez-Pamies, *The curious case of 2D isotropic incompressible Neo-Hookean composites*. Journal of Elasticity, In press (2022).
5. G.A. Francfort, A. Gloria, O. Lopez-Pamies, *Enhancement of elasto-dielectrics by homogenization of active charges*. Journal de Mathématiques Pures et Appliquées **156**, 392–419 (2021).
6. K. Ghosh, B. Shrimali, A. Kumar, O. Lopez-Pamies, *The nonlinear viscoelastic response of suspensions of rigid inclusions in rubber: I — Gaussian rubber with constant viscosity*. Journal of the Mechanics and Physics of Solids **154**, 104544 (2021).
7. K. Ghosh, O. Lopez-Pamies, *On the two-potential constitutive modeling of dielectric elastomers*. Meccanica **56**, 1505– 1521 (2021).
8. B. Shrimali, W.J. Parnell, O. Lopez-Pamies, *A simple explicit model constructed from a homogenization solution for rain mechanical response of elastomeric syntactic foams.* International Journal of Non-Linear Mechanics 126, 103548 (2020).

Center for Computational Study of Excited-State Phenomena in Energy Materials(C2SEPEM) I – Methods and Software

Lead Investigator: Steven G. Louie, sglouie@berkeley.edu.
Participating Institutions: Lawrence Berkeley National Laboratory/University of California at Berkeley (*Jeffrey B. Neaton, Jack Deslippe, Naomi Ginsberg, Eran Rabani, Feng Wang, Chao Yang*), The University of Texas, Austin (*James R. Chelikowsky*), Stanford University (*Felipe da Jornada*), University of California, Los Angeles (*Daniel Neuhauser*), Yale University (*Diana Y. Qiu*)
Source of Support: DOE-BES
Website: https://c2sepem.lbl.gov/
Keywords: First principles excited-state phenomena and spectroscopies, interacting-particle Green's functions, time-dependent and nonequilibrium phenomena, software for high-performance computing, BerkeleyGW

Project Scope

The mission of the Center for Computational Study of Excited-State Phenomena in Energy Materials (C2SEPEM) is to develop and implement new theories, methods, algorithms, and computer codes to explain and predict excited-state phenomena in materials. C2SEPEM performs research on first-principles many-body perturbation theory and advanced algorithms, as well as their experimental validation and efficient implementation for high-performance computers (HPC). Scientific research focuses on quasiparticle excitations, optical properties, time-dependent & nonequilibrium phenomena, multiparticle excitations, and exciton-phonon interactions, which are central to many fields within physics, chemistry, materials science, and engineering. This poster elucidates the vision of the center, recent methods developed to study exciton-phonon interactions, time dependent phenomena and correlation-enhanced electron phonon interactions. Software development efforts focus on improving GW workflow usability, composability and interoperability and GPU scaling in HPC systems at the exascale and beyond.

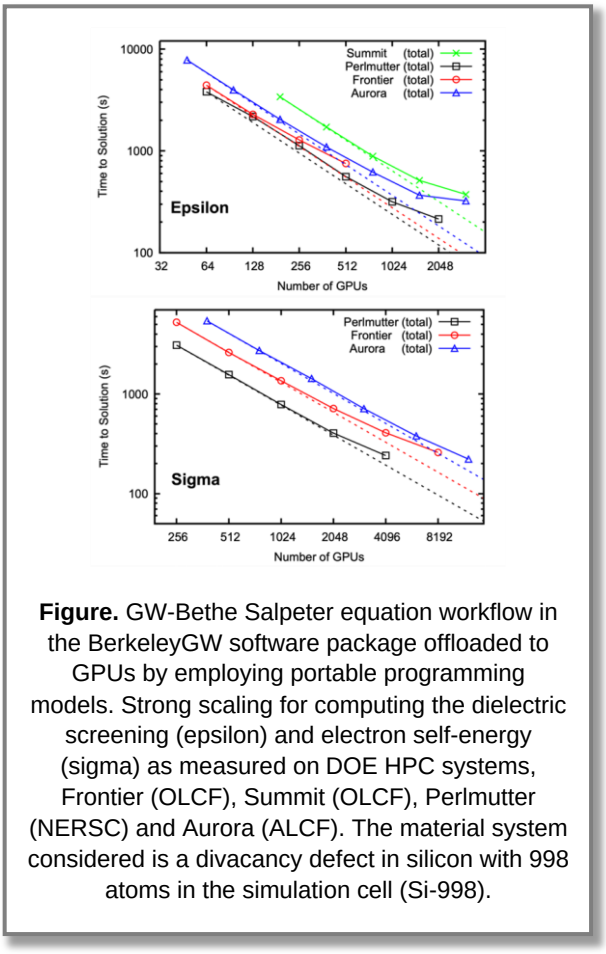


Figure. GW-Bethe Salpeter equation workflow in the BerkeleyGW software package offloaded to GPUs by employing portable programming models. Strong scaling for computing the dielectric screening (epsilon) and electron self-energy (sigma) as measured on DOE HPC systems, Frontier (OLCF), Summit (OLCF), Perlmutter (NERSC) and Aurora (ALCF). The material system considered is a divacancy defect in silicon with 998 atoms in the simulation cell (Si-998).

Relevance to MGI

Excited-state phenomena in a material typically give rise to its defining attributes and determine its usefulness. These phenomena are particularly important in processes of energy generation, transport and storage. However, *ab initio* methods for them, especially for multiple-particle correlated excitations and ultra-fast electron dynamics, have been under explored and hence limiting their studies in real materials. The methods and software developed are aiming to fill this gap, and are relevant to the predictive study of complex materials and validated through close collaboration with experimental groups. The end result will be integrated open-source software packages with capabilities to predict and understand a variety of excited-state phenomena from first principles.

Technical Progress

Technical progress of C2SEPEM covers development and release of community software packages, novel theories and methods for nonequilibrium dynamics, correlated multiparticle excitations, electron-phonon and

exciton-phonon couplings, stochastic approaches, optical phenomena in two-dimensional (2D) materials, moiré heterostructures, as well as advanced numerical algorithms and experimental studies. Over 85 papers have been published since September 2020 acknowledging support of the Center. These papers appeared in journals such as *Nature, Science, Nature Materials, Nature Nanotechnology, Nature Communications, Physical Review Letters, Nano Letters, J. American Chemical Society, ACS Nano, PNAS, Computer Physics Communications, Journal of Chemical Theory and Computation, Physical Review journals, etc*. In particular, we developed and applied advanced *ab initio* methods for ultrafast dynamics and correlated multiparticle excitations and interactions, discovered novel properties and deepened understanding of emergent quantum material systems, and scaled the software on DOE leadership class HPC resources. The team members at C2SEPEM have been recognized with several prestigious awards. We also released new software versions for BerkeleyGW (v4), StochasticGW (v3) and NanoGW. We organized annual BerkeleyGW Tutorial Workshops and the annual Berkeley Excited State Conferences, each attracting over 300 participants. This poster elucidates the vision of the center, recent methods developed to study exciton-phonon interactions, time dependent phenomena and correlation-enhanced electron phonon interactions. Software development efforts focus on improving GW workflow usability, composability and interoperability, and GPU scaling in HPC systems at the exascale and beyond.

Future Plans

We plan to further develop novel methods and codes to explore and expand the computational frontiers to excited-state phenomena that are currently inaccessible, and to enhance the applicability of existing methods to significantly broader classes of materials. Our planned directions include: 1) novel theories for excited-state phenomena; 2) new computational algorithms and their implementations; 3) porting of software packages to GPUs for exascale computing and maintaining active user and developer communities; and 4) applying developed theories and methods to study of electronic, optical, and dynamics phenomena in novel materials, in collaboration with experimental efforts.

Broader Impacts and Workforce Development

C2SEPEM values and actively engages in diversity, equity, and inclusion (DEI) initiatives. The Center strives to support researchers from underrepresented minority (URM) groups, and many of our URM alumni moved on to prominent faculty positions (e.g., Yale, Stanford, Weizmann Institute of Science, Oxford, UC Santa Barbara, USC, among others). We are actively involved in and search for funding sources for local outreach programs. Young researchers in C2SEPEM are rigorously trained in their respective disciplines; have opportunities of collaborating with peers and scientists across several different disciplines on a project; trained in and exposed to the science and art of software development; asked to take important applied math and computer science courses and instructed in best practices in writing inter-portable codes.

Data Management and Open Access

All software developed as part of C2SEPEM are made available to the community using open-source distribution licenses (the Open-Source Initiative (OSI)). The BerkeleyGW code (https://berkeleygw.org) is distributed with an open-source BSD license. Community input to the codes is solicited through workshops and meetings, and through the users' forum on the BerkeleyGW website. Many of the methods developed and the resulting codes and libraries will be general and relevant for the chemistry, condensed matter physics, materials science and engineering communities. The Center's data management framework supports the complete data lifecycle: requirements, collection, processing and validation, archiving and sharing, access and dissemination.

Advancing Along the Materials Development Continuum and Partnerships to Translation

C2SEPEM is accelerating material discovery by 1) developing *ab initio* theories and methods for excited-state properties and phenomena that are not adequately addressed for real materials from first principles currently, and 2) building state-of-the-art codes with continuous integration of new algorithms for leadership class high performance computing machines. Such methodological and code developments fill an important gap in the spectrum of tools for the theoretical and computational study of materials.

Publications

(20 most relevant recent publications acknowledging C2SEPEM)

1. M. H. Naik, E. C. Regan, Z. C. Zhang, Y. H. Chan, Z. Li, D. Wang, Y. Yoon, C. S. Ong, W. Y. Zhao, S. H. Zhao, M. I. B. Utama, B. N. Gao, X. Wei, M. Sayyad, K. Yumigeta, K. Watanabe, T. Taniguchi, S. Tongay, F. H. da Jornada, F. Wang

and S. G. Louie, *Intralayer charge-transfer moire excitons in van der Waals superlattices*, Nature **609**, 52 (2022). DOI: https://doi.org/10.1038/s41586-022-04991-9

2. M. R. Filip, D. Y. Qiu, M. Del Ben and J. B. Neaton, *Screening of Excitons by Organic Cations in Quasi-Two-Dimensional Organic–Inorganic Lead-Halide Perovskites*, *Nano Lett.* **22**, 4870 (2022). DOI: https://doi.org/10.1021/acs.nanolett.2c01306
3. J. Yin, Y. Chan, F. H. da Jornada, D. Y. Qiu, S. G. Louie and C. Yang, *Using dynamic mode decomposition to predict the dynamics of a two-time non-equilibrium Green's function*, J. of Comp. Sci. **64**, 101843 (2022). DOI: https://doi.org/10.1016/j.jocs.2022.101843
4. M. Nguyen, and D. Neuhauser, *Gapped-filtering for efficient Chebyshev expansion of the density projection operator*, Chem. Phys. Let. **806**, 140036 (2022). DOI: https://doi.org/10.1016/j.cplett.2022.140036
5. Y. Yoon, Z. Zhang, R. Qi, A. Y. Joe, R. Sailus, K. Watanabe, T. Taniguchi, S. Tongay, and F. Wang, *Charge Transfer Dynamics in $MoSe_2$/hBN/WSe_2 Heterostructures*, Nano Lett. **22**, 10140-10146 (2022). DOI: https://doi.org/10.1021/acs.nanolett.0c04955
6. A. Sood, J. B. Haber, J. Carlström, E. A. Peterson, E. Barré, J. D. Georgaras, A. H. Reid, X. Shen, M. Zajac, E. C. Regan, J. Yang, T. Taniguchi, K. Watanabe, F. Wang, X. J. Wang, J. B. Neaton, T. F. Heinz, A. M. Lindenberg, F. H. da Jornada, and A. Raja, *Bidirectional Phonon Emission in Two-Dimensional Heterostructures Triggered by Ultrafast Charge Transfer*, *Nat.* Nanotechn. 18, 29 (2022). DOI: https://doi.org/10.1038/s41565-022-01253-7
7. S. Susarla, M. H. Naik, D. D. Blach, J. Zipfel, T. Taniguchi, K. Watanabe, L. Huang, R. Ramesh, F. H. da Jornada, S. G. Louie, P. Ercius, and A. Raja, *Hyperspectral imaging of exciton confinement within a moiré unit cell with a subnanometer electron probe*, Science **378**, 1235 (2022). DOI: https://doi.org/10.1126/science.add9294
8. J. Yin, Y. Chan, F. da Jornada, D. Y. Qiu, C. Yang, and S. G. Louie, *Analyzing and predicting non-equilibrium many-body dynamics via dynamic mode decomposition*, J. of Comp. Phys. **477**, 11909 (2023). DOI: https://doi.org/10.1016/j.jcp.2023.111909
9. Y.-H. Chan, J. B. Haber, M. H. Naik, J. B. Neaton, D. Y. Qiu, Felipe H. da Jornada, and Steven G. Louie, *Exciton Lifetime and Optical Line Width Profile via Exciton–Phonon Interactions: Theory and First-Principles Calculations for Monolayer MoS2*, *Nano Lett.* **23**, 3971 (2023). DOI: https://doi.org/10.1021/acs.nanolett.3c00732
10. A. Champagne, J. B. Haber, S. Pokawanvit, D. Y. Qiu, S. Biswas, H. A. Atwater, F. H. da Jornada, and J. B. Neaton, *Quasiparticle and Optical Properties of Carrier-Doped Monolayer MoTe2 from First Principles*, Nano Lett. **23**, 4274 (2023). DOI: https://doi.org/10.1021/acs.nanolett.3c00386
11. Y. H. Chan, D. Y. Qiu, F. H. da Jornada, and S. G. Louie, *Giant self-driven exciton-Floquet signatures in time-resolved photoemission spectroscopy of MoS2 from time-dependent GW approach*, Proc. Natl. Acad. Sci. U.S.A. **120**, e2301957120 (2023). DOI: https://doi.org/10.1073/pnas.2301957120
12. J. B. Haber, D. Y. Qiu, F. H. da Jornada, and J. B. Neaton, *Maximally-localized Wannier functions for excitons in solids*, Phys. Rev. B **108**, 125118 (2023). DOI: 10.1103/PhysRevB.108.125118
13. H. L. Weaver, C. M. Went, J. Wong, D. Jasrasaria, E. Rabani, H. A. Atwater, and N. S. Ginsberg, *Detecting, Distinguishing, and Spatiotemporally Tracking Photogenerated Charge and Heat at the Nanoscale*, ACS Nano **17**, 19011 (2023). DOI: https://doi.org/10.1021/acsnano.3c04607
14. L. Mejia, J. Yin, D. R. Reichman, R. Baer, C. Yang, and E. Rabani, *Stochastic Real-Time Second-Order Green's Function Theory for Neutral Excitations in Molecules and Nanostructures*, J. Chem. Theory Comput. **19**, 5563 (2023). DOI: https://doi.org/10.1021/acs.jctc.3c00296
15. C. Hu, M. H. Naik, Y.-H. Chan, and S. G. Louie, *Excitonic interactions and mechanism for ultrafast interlayer photoexcited response in van der Waals heterostructures*, Phys. Rev. Lett. **131**, 236904 (2023). DOI: 10.1103/PhysRevLett.131.236904
16. C. Hu, M. H. Naik, Y.-H. Chan, J.-W. Ruan and S. G. Louie, *Light-induced shift current vortex crystals in moiré heterobilayers*, Proc. Natl. Acad. Sci. U.S.A. **120**, e2314775120 (2023). DOI: https://doi.org/10.1073/pnas.2314775120
17. S. Biswas, A. Champagne, J. B. Haber, S. Pokawanvit, J. Wong, H. Akbari, S. Krylyuk, K. Watanabe, T. Taniguchi, A. V. Davydov, Z. Y. Al Balushi, D. Y. Qiu, F. H. da Jornada, J. B. Neaton, and H. A. Atwater, *Rydberg Excitons in Monolayer MoTe2*, ACS Nano **17**, 7685 (2023). DOI: https://doi.org/10.1021/acsnano.3c00145
18. R. Altman, S. K. Kundu, and F. H. da Jornada, *Mixed Stochastic-Deterministic Approach for Many-Body Perturbation Theory Calculations*, Phys. Rev. Lett. **132**, 0864401 (2024). DOI: 10.1103/PhysRevLett.132.086401
19. W. Gao, Z. Tang, J. Zhao, J. R. Chelikowsky, *Efficient Full-frequency GW Calculations using a Lanczos Method*, Phys. Rev. Lett. **132**, 126402 (2024). DOI: 10.1103/PhysRevLett.132.126402
20. H.-Y. Li, Z.-Y. Xiang, Mit H. Naik, W.-C. Kim, Z.-L. Li, R. Sailus, R. Banerjee, T. Taniguchi, K. Watanabe, S. Tongay, Alex Zettl, F. H. da Jornada, S. G. Louie, M. F. Crommie and F. Wang, *Imaging Moiré Excited States with Photocurrent Tunneling Microscopy*, Nat. Mat. **23**, 633 (2024). DOI: https://doi.org/10.1038/s41563-023-01753-4

Center for Computational Study of Excited-State Phenomena in Energy Materials (C2SEPEM) II – Theory and Validation

Lead Investigator: Steven G. Louie, sglouie@berkeley.edu.
Participating Institutions: Lawrence Berkeley National Laboratory/University of California at Berkeley (*Jeffrey B. Neaton, Jack Deslippe, Naomi Ginsberg, Eran Rabani, Feng Wang, Chao Yang*), The University of Texas, Austin (*James R. Chelikowsky*), Stanford University (*Felipe da Jornada*), University of California, Los Angeles (*Daniel Neuhauser*), Yale University (*Diana Y. Qiu*)
Source of Support: DOE-BES
Website: https://c2sepem.lbl.gov/
Keywords: First principles excited-state phenomena and spectroscopies, interacting-particle Green's functions, time-dependent and nonequilibrium phenomena, software for high-performance computing, BerkeleyGW

Project Scope

The mission of the Center for Computational Study of Excited-State Phenomena in Energy Materials (C2SEPEM) is to develop and implement new theories, methods, algorithms, and computer codes to explain and predict excited-state phenomena in materials. C2SEPEM performs research on first-principles many-body perturbation theory and advanced algorithms, as well as their experimental validation and efficient implementation for high-performance computers (HPC). Scientific research focuses on quasiparticle excitations, optical properties, time-dependent & nonequilibrium phenomena, multiparticle excitations, and exciton-phonon interactions, which are central to many fields within physics, chemistry, materials science, and engineering. Software development focuses on open-access with interoperability and scaling to HPC systems.

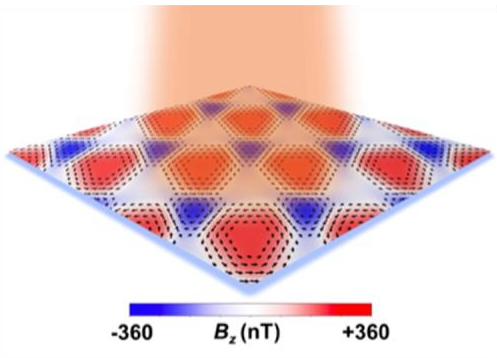


Figure. Photoexcited shift current vortex crystal in a WS_2/WSe_2 moiré superlattice. Arrows indicate the DC photocurrent density, and colors denote the out-of-plane magnetic field intensity [16].

Relevance to MGI

Excited-state phenomena in a material typically give rise to its defining attributes and determine its usefulness. These phenomena are particularly important in processes of energy generation, transport and storage. However, *ab initio* methods for them, especially for multiple-particle correlated excitations and ultra-fast electron dynamics, have been under explored and hence limiting their studies in real materials. The methods and software developed are aiming to fill this gap, and are relevant to the predictive study of complex materials and validated through close collaboration with experimental groups. The end result will be integrated open-source software packages with capabilities to predict and understand a variety of excited-state phenomena from first principles.

Technical Progress

Technical progress of C2SEPEM covers development and release of community software packages, novel theories and methods for nonequilibrium dynamics, correlated multiparticle excitations, electron-phonon and exciton-phonon couplings, stochastic approaches, optical phenomena in two-dimensional (2D) materials, moiré heterostructures, as well as advanced numerical algorithms and experimental studies. Over 85 papers have been published since September 2020 acknowledging support of the Center. These papers appeared in journals such as *Nature, Science, Nature Materials, Nature Nanotechnology, Nature Communications, Physical Review Letters, Nano Letters, J. American Chemical Society, ACS Nano, PNAS, Computer Physics Communications, Journal of Chemical Theory and Computation, Physical Review journals, etc*. In particular, we developed and applied advanced *ab initio* methods for ultrafast dynamics and correlated multiparticle excitations and interactions, discovered novel properties and deepened understanding of emergent quantum material systems, and scaled the

software on DOE leadership class HPC resources. The team members at C2SEPEM have been recognized with several prestigious awards. We also released new software versions for BerkeleyGW (v4), StochasticGW (v3) and NanoGW. We organized annual BerkeleyGW Tutorial Workshops and the annual Berkeley Excited State Conferences, each attracting over 300 participants. This poster highlights theory developments and their experimental validation in the center with a focus on applications in twisted moiré materials, nonlinear optical spectroscopy in the perturbative and strong-field regimes, multi-particle excitations, and self-energy-driven Floquet phenomena.

Future Plans

We plan to further develop novel methods and codes to explore and expand the computational frontiers to excited-state phenomena that are currently inaccessible, and to enhance the applicability of existing methods to significantly broader classes of materials. Our planned directions include: 1) novel theories for excited-state phenomena; 2) new computational algorithms and their implementations; 3) porting of software packages to GPUs for exascale computing and maintaining active user and developer communities; and 4) applying developed theories and methods to study of electronic, optical, and dynamics phenomena in novel materials, in collaboration with experimental efforts.

Broader Impacts and Workforce Development

C2SEPEM values and actively engages in diversity, equity, and inclusion (DEI) initiatives. The Center strives to support researchers from underrepresented minority (URM) groups, and many of our URM alumni moved on to prominent faculty positions (e.g., Yale, Stanford, Weizmann Institute of Science, Oxford, UC Santa Barbara, USC, among others). We are actively involved in and search for funding sources for local outreach programs. Young researchers in C2SEPEM are rigorously trained in their respective disciplines; have opportunities of collaborating with peers and scientists across several different disciplines on a project; trained in and exposed to the science and art of software development; asked to take important applied math and computer science courses and instructed in best practices in writing inter-portable codes.

Data Management and Open Access

All software developed as part of C2SEPEM are made available to the community using open-source distribution licenses (the Open-Source Initiative (OSI)). The BerkeleyGW code (https://berkeleygw.org) is distributed with an open-source BSD license. Community input to the codes is solicited through workshops and meetings, and through the users' forum on the BerkeleyGW website. Many of the methods developed and the resulting codes and libraries will be general and relevant for the chemistry, condensed matter physics, materials science and engineering communities. The Center's data management framework supports the complete data lifecycle: requirements, collection, processing and validation, archiving and sharing, access and dissemination.

Advancing Along the Materials Development Continuum and Partnerships to Translation

C2SEPEM is accelerating material discovery by 1) developing *ab initio* theories and methods for excited-state properties and phenomena that are not adequately addressed for real materials from first principles currently, and 2) building state-of-the-art codes with continuous integration of new algorithms for leadership class high performance computing machines. Such methodological and code developments fill an important gap in the spectrum of tools for the theoretical and computational study of materials.

Publications

(20 most relevant recent publications acknowledging C2SEPEM)

1. M. H. Naik, E. C. Regan, Z. C. Zhang, Y. H. Chan, Z. Li, D. Wang, Y. Yoon, C. S. Ong, W. Y. Zhao, S. H. Zhao, M. I. B. Utama, B. N. Gao, X. Wei, M. Sayyad, K. Yumigeta, K. Watanabe, T. Taniguchi, S. Tongay, F. H. da Jornada, F. Wang and S. G. Louie, *Intralayer charge-transfer moire excitons in van der Waals superlattices*, Nature **609**, 52 (2022). DOI: https://doi.org/10.1038/s41586-022-04991-9
2. M. R. Filip, D. Y. Qiu, M. Del Ben and J. B. Neaton, *Screening of Excitons by Organic Cations in Quasi-Two-Dimensional Organic–Inorganic Lead-Halide Perovskites*, *Nano Lett.* **22**, 4870 (2022). DOI: https://doi.org/10.1021/acs.nanolett.2c01306

3. J. Yin, Y. Chan, F. H. da Jornada, D. Y. Qiu, S. G. Louie and C. Yang, *Using dynamic mode decomposition to predict the dynamics of a two-time non-equilibrium Green's function*, J. of Comp. Sci. **64**, 101843 (2022). DOI: https://doi.org/10.1016/j.jocs.2022.101843
4. M. Nguyen, and D. Neuhauser, *Gapped-filtering for efficient Chebyshev expansion of the density projection operator*, Chem. Phys. Let. **806**, 140036 (2022). DOI: https://doi.org/10.1016/j.cplett.2022.140036
5. Y. Yoon, Z. Zhang, R. Qi, A. Y. Joe, R. Sailus, K. Watanabe, T. Taniguchi, S. Tongay, and F. Wang, *Charge Transfer Dynamics in $MoSe_2$/hBN/WSe_2 Heterostructures*, Nano Lett. **22**, 10140-10146 (2022). DOI: https://doi.org/10.1021/acs.nanolett.0c04955
6. A. Sood, J. B. Haber, J. Carlström, E. A. Peterson, E. Barré, J. D. Georgaras, A. H. Reid, X. Shen, M. Zajac, E. C. Regan, J. Yang, T. Taniguchi, K. Watanabe, F. Wang, X. J. Wang, J. B. Neaton, T. F. Heinz, A. M. Lindenberg, F. H. da Jornada, and A. Raja, *Bidirectional Phonon Emission in Two-Dimensional Heterostructures Triggered by Ultrafast Charge Transfer*, *Nat.* Nanotechn. 18, 29 (2022). DOI: https://doi.org/10.1038/s41565-022-01253-7
7. S. Susarla, M. H. Naik, D. D. Blach, J. Zipfel, T. Taniguchi, K. Watanabe, L. Huang, R. Ramesh, F. H. da Jornada, S. G. Louie, P. Ercius, and A. Raja, *Hyperspectral imaging of exciton confinement within a moiré unit cell with a subnanometer electron probe*, Science **378**, 1235 (2022). DOI: https://doi.org/10.1126/science.add9294
8. J. Yin, Y. Chan, F. da Jornada, D. Y. Qiu, C. Yang, and S. G. Louie, *Analyzing and predicting non-equilibrium many-body dynamics via dynamic mode decomposition*, J. of Comp. Phys. **477**, 11909 (2023). DOI: https://doi.org/10.1016/j.jcp.2023.111909
9. Y.-H. Chan, J. B. Haber, M. H. Naik, J. B. Neaton, D. Y. Qiu, Felipe H. da Jornada, and Steven G. Louie, *Exciton Lifetime and Optical Line Width Profile via Exciton–Phonon Interactions: Theory and First-Principles Calculations for Monolayer MoS2*, *Nano Lett.* **23**, 3971 (2023). DOI: https://doi.org/10.1021/acs.nanolett.3c00732
10. A. Champagne, J. B. Haber, S. Pokawanvit, D. Y. Qiu, S. Biswas, H. A. Atwater, F. H. da Jornada, and J. B. Neaton, *Quasiparticle and Optical Properties of Carrier-Doped Monolayer MoTe2 from First Principles*, Nano Lett. **23**, 4274 (2023). DOI: https://doi.org/10.1021/acs.nanolett.3c00386
11. Y. H. Chan, D. Y. Qiu, F. H. da Jornada, and S. G. Louie, *Giant self-driven exciton-Floquet signatures in time-resolved photoemission spectroscopy of MoS2 from time-dependent GW approach*, Proc. Natl. Acad. Sci. U.S.A. **120**, e2301957120 (2023). DOI: https://doi.org/10.1073/pnas.2301957120
12. J. B. Haber, D. Y. Qiu, F. H. da Jornada, and J. B. Neaton, *Maximally-localized Wannier functions for excitons in solids*, Phys. Rev. B **108**, 125118 (2023). DOI: 10.1103/PhysRevB.108.125118
13. H. L. Weaver, C. M. Went, J. Wong, D. Jasrasaria, E. Rabani, H. A. Atwater, and N. S. Ginsberg, *Detecting, Distinguishing, and Spatiotemporally Tracking Photogenerated Charge and Heat at the Nanoscale*, ACS Nano **17**, 19011 (2023). DOI: https://doi.org/10.1021/acsnano.3c04607
14. L. Mejia, J. Yin, D. R. Reichman, R. Baer, C. Yang, and E. Rabani, *Stochastic Real-Time Second-Order Green's Function Theory for Neutral Excitations in Molecules and Nanostructures*, J. Chem. Theory Comput. **19**, 5563 (2023). DOI: https://doi.org/10.1021/acs.jctc.3c00296
15. C. Hu, M. H. Naik, Y.-H. Chan, and S. G. Louie, *Excitonic interactions and mechanism for ultrafast interlayer photoexcited response in van der Waals heterostructures*, Phys. Rev. Lett. **131**, 236904 (2023). DOI: 10.1103/PhysRevLett.131.236904
16. C. Hu, M. H. Naik, Y.-H. Chan, J.-W. Ruan and S. G. Louie, *Light-induced shift current vortex crystals in moiré heterobilayers*, Proc. Natl. Acad. Sci. U.S.A. **120**, e2314775120 (2023). DOI: https://doi.org/10.1073/pnas.2314775120
17. S. Biswas, A. Champagne, J. B. Haber, S. Pokawanvit, J. Wong, H. Akbari, S. Krylyuk, K. Watanabe, T. Taniguchi, A. V. Davydov, Z. Y. Al Balushi, D. Y. Qiu, F. H. da Jornada, J. B. Neaton, and H. A. Atwater, *Rydberg Excitons in Monolayer MoTe2*, ACS Nano **17**, 7685 (2023). DOI: https://doi.org/10.1021/acsnano.3c00145
18. R. Altman, S. K. Kundu, and F. H. da Jornada, *Mixed Stochastic-Deterministic Approach for Many-Body Perturbation Theory Calculations*, Phys. Rev. Lett. **132**, 0864401 (2024). DOI: 10.1103/PhysRevLett.132.086401
19. W. Gao, Z. Tang, J. Zhao, J. R. Chelikowsky, *Efficient Full-frequency GW Calculations using a Lanczos Method*, Phys. Rev. Lett. **132**, 126402 (2024). DOI: 10.1103/PhysRevLett.132.126402
20. H.-Y. Li, Z.-Y. Xiang, Mit H. Naik, W.-C. Kim, Z.-L. Li, R. Sailus, R. Banerjee, T. Taniguchi, K. Watanabe, S. Tongay, Alex Zettl, F. H. da Jornada, S. G. Louie, M. F. Crommie and F. Wang, *Imaging Moiré Excited States with Photocurrent Tunneling Microscopy*, Nat. Mat. **23**, 633 (2024). DOI: https://doi.org/10.1038/s41563-023-01753-4

Collaborative Research: DMREF: Accelerated Design of Redox-Active Polymers for Metal-Free Batteries

Lead Investigator: Jodie L. Lutkenhaus (jodie.lutkenhaus@tamu.edu), Juan de Pablo (depablo@uchicago.edu), Stuart Rowan (stuartrowan@uchicago.edu), and Daniel Tabor (daniel_tabor@tamu.edu)
Participating Institutions: Texas A&M University and University of Chicago
Source of Support: NSF DMREF-2119672/2119673
Website: none
Keywords: Phthalimide-based batteries, multiscale modeling, molecular dynamics, all organic batteries, organic mixed conductors

Project Scope

The project has two main thrusts: "Multiscale Design of Polyphthalimides" and "Redox-Active Chemical Space Exploration." The first focuses on designing new electrochemically active phthalimide materials in solution and solid-state through the integration of computational design and experiments. The second expands chemical space exploration and design principles for anodic and cathodic materials, depositing data and workflows in open-access databases.

Relevance to MGI

This project directly integrates 1) inverse chemical design tools, 2) high-throughput multiscale computational simulations, 3) new methods for representing and designing polymers, and 4) the large-scale open-access storage of computational data, code to execute new computational methods, and experimental outcomes. Each thrust within the collaboration contains direct feedback loops between experimental and computational results.

Technical progress

- **Solid-State Phthalimide-Containing Polymers for All-Organic Batteries.** We predict the structural, ionic, and electronic properties of anodic phthalimide-containing polymers using a multiscale approach combining molecular dynamics, electronic structure calculations, and machine learning models. This method bridges molecular characteristics with macroscopic properties such as electron transport diffusion coefficients (D_{app}). Our recent study reveals that the state of charge significantly influences solid-state packing, affecting ionic and electronic transport. We predict three orders of magnitude increase in D_{app} ($\approx 10^{-6}$ cm^2 s^{-1}) for phthalimide-based polymers compared to a nitroxide radical-based polymer, highlighting their potential as redox-active materials in all-organic batteries.
- **Redox Activity of Phthalimide-Based Polymers in Solution.** With the goal of understanding inter vs. intra-chain electron transfer in the phthalimide-based polymers mentioned above, we compare different concentrations of polymers with two different backbones. The dissolved polymers exhibit a diffusion-limited redox reaction. The overlap concentration for each polymer was identified, and the reaction kinetics were found to vary accordingly. Both polymers, regardless of backbone flexibility, exhibited the same trends with concentration.

- **Phthalimide Copolymers for Enhanced Charge Transport and Stability.** We have synthesized glycidyl methacrylate-phthalimide copolymers to improve charge transport and stability. The copolymer's redox behavior and kinetic parameters will be analyzed, and it will be used to create a composite electrode for further electrochemical studies. Ion transport will be investigated using advanced techniques, guided by our multiscale modeling framework.

Future Plans

- **Developing New Cathodic Materials.** We will refine generative design workflows to produce stable, redox-active molecules, focusing on phenothiazine-based polymers.
- **Phthalimide Units with Increased Stability.** Identified stable phthalimide derivatives will be validated and optimized through electrochemical tests and multiscale polymer MD simulations, including phthalimide copolymers.
- **Active Learning for Material Discovery.** We will use active learning, including Bayesian optimization and molecular representations, to explore chemical space and discover new redox-active polymers.

Broader Impacts and Workforce Development

Our project supports the MGI philosophy by developing the student workforce and advancing materials data usage through advanced computational and experimental tools. Over the past year, we have trained 13 individuals (7 Ph.D. students, 3 postdocs, 3 undergraduates) in interdisciplinary skills. They presented insights at 12 conferences, including 5 public talks, and engaged in public outreach, reaching 900 people. Our principal investigators were invited to speak at 3 major events. Our work on organic, polymer-based batteries reduces reliance on scarce metals like lithium and cobalt, promoting recyclable energy storage and minimizing environmental impact.

Data Management and Open Access

Our polymer sample's properties vary due to inconsistent synthesis and characterization conditions, complicating replication. To improve reproducibility and accessibility, we are integrating data and workflows into CRIPT. This platform stores procedures, AI models, and measurements, mapping processes from inputs to outputs. Our team, trained to use CRIPT's tools, is actively contributing to its development and uploading data to confirm its effectiveness.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We are using ML-driven molecular design to highlight promising redox-active molecules for experimentation, and we are using high-throughput machines to iterate over polymer design spaces to elucidate polymer-electrochemical relationships. Our project has gathered data from existing literature and our own work that we are uploading into CRIPT (Community Resource for Innovation in Polymer Technology) to become the first organic redox-active polymer open-access database. Moreover, multiscale models of the polymers have been already made open access via GitHub (https://github.com/ricalessandri/redox-active-polymers). One of the hurdles we seek to overcome is developing high throughput electrochemical characterization platforms to complement our computation and synthesis.

Publications and References

1. Alessandri R, Li C-H, Keating S, Mohanty KT, Peng A, Lutkenhaus JL, Rowan SJ, Tabor DP, de Pablo JJ, *Structural, Ionic, and Electronic Properties of Solid-State Phthalimide-Containing Polymers for All-Organic Batteries,* JACS Au **4** 2300–2311 (2024). DOI: https://doi.org/10.1021/jacsau.4c00276
2. Ma T, Li C-H, Thakur RH, Tabor DP, Lutkenhaus JL, *The role of the electrolyte in non-conjugated radical polymers for metal-free aqueous energy storage electrodes*, Nat. Mater. **22**, 495-502 (2023). DOI: https://doi.org/10.1038/s41563-023-01518-z
3. Li C-H, Tabor DP, *Reorganization Energy Predictions with Graph Neural Networks Informed by Low-Cost Conformers,* J. Phys. Chem. A **127** 3484-3489 (2023). DOI: https://doi.org/10.1021/acs.jpca.2c09030
4. Ma T, Fox E, Li C-H, Niradha Sachithani KA, Mohanty K, Tabor DP, Pentzer EB, Lutkehnahus JL, *Charge Transfer in Spatially Defined Organic Radical Polymers*, Chem. Mater. **35**, 9346-9351 (2023). DOI: https://doi.org/10.1021/acs.chemmater.3c02148
5. Alessandri R, de Pablo JJ, *Prediction of Electronic Properties of Radical-Containing Polymers at Coarse-Grained Resolutions*, Macromolecules **56**, 3574-3584 (2023). DOI: https://doi.org/10.1021/acs.macromol.3c00141
6. Easley AD, Mohanty K, Lutkenhaus JL, *Water-coupled monovalent and divalent ion transport in polyviologen networks*, J. Mater. Chem. A **11**, 8783-8790 (2023). DOI: https://doi.org/10.1039/D3TA00289F
7. Shi Y, Mudugamuwa CJ, Abeysinghe TN, Alotaibi YSM, Monteiro MJ, Chalker JM, Lutkenhaus JL, Jia Z, *Ionic Effect on Electrochemical Behavior of Water-Soluble Radical Polyelectrolytes,* Macromolecules **55**, 5733-5743 (2022). DOI: https://doi.org/10.1021/acs.macromol.2c00519

Informed Design of Epitaxial Organic Electronics and Photonics

Lead Investigator: Noa Marom, nmarom@andrew.cmu.edu
Participating Institutions: Carnegie Mellon University, Princeton University, University of Michigan
Source of Support: NSF
Website: None
Keywords: Organic electronics, organic epitaxy, electronic structure, machine learning, interfaces

Project Scope

We aim to develop the computational and experimental tools needed to grow epitaxial crystalline molecular heterostructures, demonstrate them experimentally, and explore the resulting physics and application possibilities. This work would open up a new direction in the field of organic electronics and deliver a new materials platform for more efficient organic solar cells and transistors and for on-chip integrated photonics. We use a synergistic approach that integrates first principles simulations and machine leanring (ML) with a combination of high- and low-throughput experiments in a feedback loop.

Relevance to MGI

This research accelerates materials discovery and development by building the fundamental knowledge base needed to design and make integrated organic and hybrid electronic and photonic devices with specific desired properties and functionalities, based on crystalline materials that form ordered, high-quality epitaxial interfaces. Our interdisciplinary team of experimentalists and theorists works in a "closed loop". Simulations inform efforts to discover new materials combinations and realize epitaxial organic interfaces with better electronic and optical properties. Simulations begin at the ab initio atomistic length scale. Data is used to train ML interatomic potentials (MLPs) that reach quantum mechanical accuracy with classical force field speed, and predict materials structure and properties. Automated high-throughput experiments will be conducted to acquire data to train ML models. Growth, characterization, and device fabrication is performed for the most promising candidates predicted by simulations. Experimental verification informs the development of computational methods.

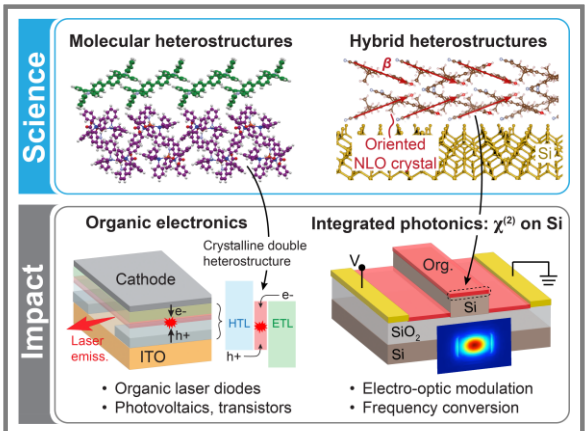


Figure 1. Major scientific thrusts and their potential technological impact. Epitaxial molecular heterostructures would enable organic laser diodes and higher mobility transistors. (Quasi-)epitaxial growth of acentric nonlinear optical (NLO) crystals on, e.g. Si, could provide a path to achieve large χ(2) optical nonlinearity in integrated photonics.

Technical Progress

The organic-on-inorganic heteroepitaxy thrust has focused on growing second order nonlinear optical organic crystal films on silicon. This could provide a versatile, monolithic, and back-end-of-line-compatible route to high $\chi^{(2)}$ on-chip integrated photonics. We demonstrated growth of large (> 100 μm) single crystal domains of the nonlinear molecule OH1 on glass and Si by vacuum evaporation followed by short thermal annealing. The crystallites are tens of nm thick and exhibit strong second harmonic generation with their primary $\chi^{(2)}$ tensor component lying predominantly in plane. Calculations support the observed crystallite orientation and rationalize the origin of a new optical transition that emerges in the OH1 crystallites. A single domain can grow uninterrupted through several adjacent, lithographically-defined channels, opening up a path to exploit OH1 in $\chi^{(2)}$-based Si photonic devices such as electro-optic modulation, frequency conversion, and photon pair generation [1].

The organic-organic heteroepitaxy thrust has focused on discovery of materials that can serve as substrates, which requires the formation of large crystalline platelets. Molecular crystals that form platelet morphology feature both high melting point (T_m) and crystallization driving force (ΔG_c). We developed ML models to predict these properties in order to identify candidate organic materials with the potential to crystallize into platelets. Six organic molecules identified by the ML algorithm were experimentally evaluated; three crystallized as platelets, one crystallized as a spherulite, and two resisted crystallization. This demonstrates the success of ML for predicting thermal properties of organic semiconductors and reinforces the use of T_m and ΔG_c as predictive descriptors [2].

We continue to develop the Genarris-Interfaces code for structure prediction of molecular interfaces. Interface structures are generated by first using epitaxy matrices to construct all the possible substrate surface cells up to a user-defined area and then generating film structures in all the layer groups compatible with the number of molecules per cell and the symmetry of commensurate substrate cells (Fig. 2a). The code has been applied successfully to several organic films on coinage metals and produced structures in close agreement with experimental STM images, shown here for PTCDA/Ag (Fig. 2b).

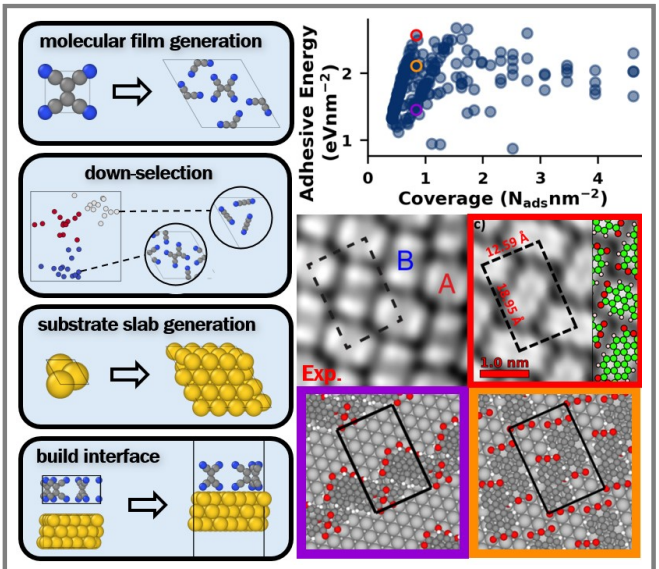


Figure 2. Structure prediction of organic/inorganic interfaces with Genarris. Left: workflow of interface structure generation. Top right: Adhesion energy vs. coverage for PTCDA/Ag structures generated by Genarris. Bottom right: STM image [3] compared to STM simulation of the structure circled in red, which is the most stable in the experimental coverage bin. Two other, less stable structures are also shown.

Future Plans

Work on hybrid organic-inorganic crystalline interfaces will exploit surface interactions and growth conditions to make larger OH1 crystallites with controlled in-plane orientation. We will leverage photoalignment layers used to align liquid crystals in displays. Simulations and ML models will help identify underlayer materials that hydrogen bond with OH1, possess a high glass transition temperature, and can be oriented optically in order to systematically overcome the orientation challenge. This would enable a wide range of integrated photonic devices.

The computational thrust will continue to work on the development of ML models for predicting crystallization propensity with the help of automated high-throughput experiments and on the development of algorithms for interface structure prediction and MLPs that work for interfaces.

Broader Impacts and Workforce Development

This project trains students in an interdisciplinary environments and imparts skills that are in high demand in the job market. In its first year this project has supported 4 junior participants, 3 of whom are women (one Hispanic), and a URM undergraduate. We plan to drive progress in this nascent field by organizing workshops and conference symposia to nucleate a community of researchers including experimentalists, theorists, and data scientists.

Data Management and Open Access

We plan to make data and codes developed within this project publicly available according to the FAIR standards. Open source codes developed by Marom's group are available at: https://www.noamarom.com/software/download/. All data, ML models and codes developed by the Isayev's group are available at https://github.com/isayevlab.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We envision the project's outputs, including new computational approaches and device concepts being adopted, integrated, or otherwise deployed for the development of optoelectronic and photonic technologies based on crystalline molecular films. We actively pursue industry collaborations and follow-on funding from more applied sources. Marom has recently signed a contract with Meta to utilize some of the computational techniques developed within this project for the discovery of materials for organic displays.

Publications and References

1. N. Krainova, H.M. Johnson, R. Lampande, S. Gao, N. Marom, B.P. Rand, and N.C. Giebink, Vacuum deposition of $\chi^{(2)}$ nonlinear organic single crystal films on silicon. *Appl. Phys. Lett.* **in press** (2024)
2. H. M. Johnson, F. Gusev, J. T. Dull, Y. Seo, R. D. Priestley, O. Isayev, and B. P. Rand, Discovery of Crystallizable Organic Semiconductors with Machine Learning. *JACS* **in press** (2024)
3. A. Sabitova, R. Temirov, and F. S. Tautz. Lateral scattering potential of the PTCDA/Ag(111) interface state. *Phys. Rev. B* 98, 205429 (2018)

Autonomous Experimentation for Nanotube Synthesis

Lead Investigator: Benji Maruyama, Benji.Maruyama@afrl.af.mil
Participating Institutions: Air Force Research Laboratory
Source of Support: AFRL, AFOSR.
Website: None
Keywords: AMII, Autonomous Experimentation, Carbon Nanotubes, Hypothesis-Driven

Project Scope

Carbon nanotubes (CNTs) are a promising material with myriad applications, including conventional and flexible electronics, and their strength to weight ratio makes them an ideal component in structural composite materials. Despite more than two decades of development as a high-performance material [8], CNT synthesis remains a poorly understood process, due in part to the slow pace of research: Typically 1-2 experiments per day. Understanding of CNT growth has increased tremendously due to experimental and computational efforts, but faster, hypothesis-driven, iterative search is required for further understanding, ultimately leading to commercialization.

Relevance to MGI

ARES is the pioneering effort for Autonomous Experimentation in Materials[2, 3], and ARES is highlighted in the 2021 MGI Strategic Plan[4]. This effort exploits hypothesis-driven search using metallurgical thermodynamics of oxidation/reduction to optimize catalyst activity.

Technical Progress

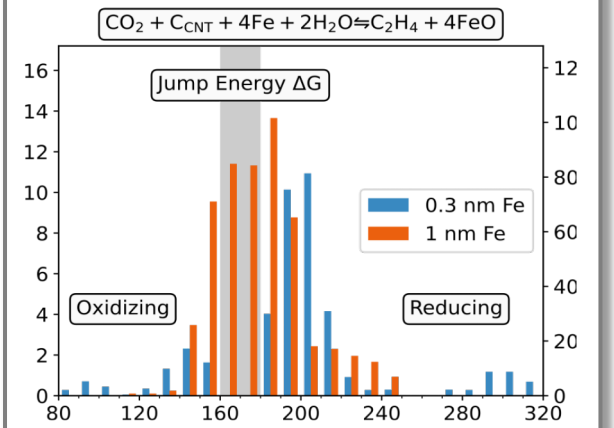


Figure. We report a new understanding that iron carbon nanotube catalysts are most active at the transition between oxidized and reduced state, with peak nanotube yield, diameter control, and catalyst lifetime. To confirm this hypothesis, we used a novel jump regression AI method that directly and efficiently target the discontinuous phase transformation in our autonomous experimentation system[1].

Catalyst control is critical to carbon nanotube (CNT) growth and scaling their production. In supported catalyst CNT growth, the reduction of an oxidized metal catalyst enables growth, but its reduction also initiates catalyst deactivation via Ostwald ripening. Here, we conducted autonomous experiments guided by a hypothesis-driven machine learning planner based on a novel jump regression algorithm. This planning algorithm iteratively models the experimental response surface to identify discontinuities, such as those created by a material phase change, and targets further experiments to improve the fit and reduce uncertainty in its model. This approach led us to identify conditions that resulted in the greatest CNT yields as a function of the driving forces of catalyst reduction in a fraction of the time and cost of conventional experimental approaches. By varying temperature and the reducing potential of the growth atmosphere, we identified discontinuous jumps in CNT growth for two thicknesses of an iron catalyst, resulting in largest observed yields in narrow and distinct regions of thermodynamic space where we believe the reduced catalyst is in equilibrium with its oxide. At these jumps, we also observed the longest growth lifetimes and a greater degree of diameter control. We believe that conducting CNT growth at these conditions optimizes

catalyst activity by inhibiting Ostwald ripening-induced deactivation, thereby keeping catalyst nanoparticles smaller and more numerous. This work establishes a thermodynamic framework for a generalized understanding of metal catalysts in CNT growth, and demonstrates the capability of iterative, hypothesis-driven autonomous experimentation to greatly accelerate materials science[1].

Future Plans

We plan to generalize our thermodynamic model of catalyst activity to other catalyst elements and compounds. We also plan to generalize the environmental response to other growth gases, and finally understand the effect of catalyst/support interactions via catalyst thickness.

Broader Impacts and Workforce Development

We are building an Educational ARES effort to directly address the AI gap that impacts disadvantaged groups. Educational ARES aims to build access and expertise in underrepresented groups for AI and autonomous experimentation.

Data Management and Open Access

Autonomous Experimentation Systems have the unique advantage that the data can be born "FAIR". Our Educational ARES 3D printer has the ability to expose data immediately upon generation, including materials results, planner data and analysis data. Additionally, our ARES OS 2.0 software is open source: [https://github.com/AFRL-ARES/AresLib].

Advancing Along the Materials Development Continuum and Partnerships to Translation

We plan to exploit our fundamental understanding to scale CNT synthesis. In particular, using methane pyrolysis, we have the potential to impact global warming by co-generation of clean hydrogen and CNT materials for structures, energy storage and low-CO_2 cement.

Publications and References

(1) Waelder, R.; Park, C.; Sloan, A.; Carpena-Núñez, J.; Yoho, J.; Gorsse, S.; Rao, R.; Maruyama, B. Improved understanding of carbon nanotube growth via autonomous jump regression targeting of catalyst activity. *Carbon* **2024**, 119356.
(2) Nikolaev, P.; Hooper, D.; Webber, F.; Rao, R.; Decker, K.; Krein, M.; Poleski, J.; Barto, R.; Maruyama, B. Autonomy in materials research: a case study in carbon nanotube growth. *npj Computational Materials* **2016**, *2* (1), 1-6.
(3) Stach, E.; DeCost, B.; Kusne, A. G.; Hattrick-Simpers, J.; Brown, K. A.; Reyes, K. G.; Schrier, J.; Billinge, S.; Buonassisi, T.; Foster, I.; et al. Autonomous experimentation systems for materials development: A community perspective. *Matter* **2021**, *4* (9), 2702-2726. DOI: 10.1016/j.matt.2021.06.036.
(4) Christodoulou, J.; Friedersdorf, L. E.; Sapochak, L.; Warren, J. A. The second decade of the materials genome initiative. *JOM* **2021**, *73* (12), 3681-3683.

Designing Plasmonic Nanoparticle Assemblies For Active Nanoscale Temperature Control By Exploiting Near- And Far-Field Coupling

Lead Investigator: David J. Masiello, masiello@uw.edu
Participating Institutions: University of Washington, Temple University, University of Illinois Urbana-Champaign
Source of Support: NSF-DMREF
Website: https://faculty.washington.edu/masiello/dmref/
Keywords: plasmon lattices, photothermal heating, momentum-resolved spectroscopy, nanophotonics, plasmonics

Project Scope

The goal of this research is to overcome thermal diffusion through the theoretical design and experimental realization of a new class of plasmonic nano-patterned metamaterials capable of realizing actively controllable steady-state thermal gradients spanning from the nano- (≲100 nm) to micron- (1-1000 μm) scales by exploiting the photothermal conversion properties of lattice plasmon resonances in diffractively coupled nanoparticle arrays. We aim to 1) predict and fabricate 2D periodic plasmonic Bravais lattices capable of generating specific long- range (1-1000 μm) thermal profiles at various spatial locations using different excitation wavelengths in the visible and near-IR spectral ranges combined with different angles of incidence and polarization states of light, and 2) extend to 2D periodic non-Bravais plasmonic dimer lattices to control the thermal profile within each unit cell (≲100 nm) in addition to the long range global temperature control introduced by coupling light into the lattice's diffractive modes. This work also requires careful examination of the photothermal responses of individual plasmonic nanoparticles (which form the basic elements of our plasmonic lattices) in the regime where they are large enough to both absorb and scatter, using single-particle photothermal absorption spectroscopy techniques.

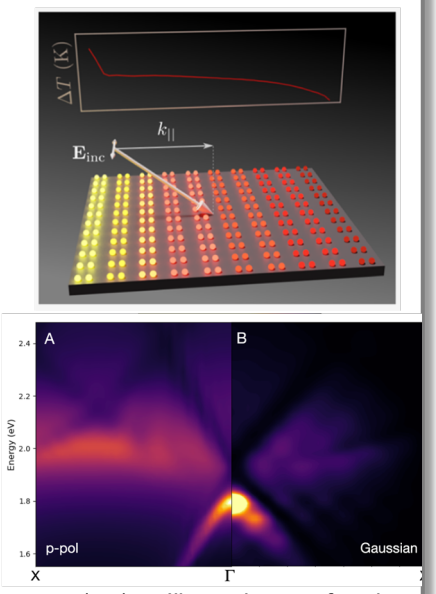


Figure. (top) Illustration of the photothermal response of a plasmon lattice under optical illumination as a function of frequency, polarization, and wave vector. (lower) Comparison of the momentum-resolved optical spectra of a plasmon lattice under (A) p-polarized plane wave excitation in a wide-field illumination geometry versus (B) a focused Gaussian beam illumination geometry.

Relevance to MGI

Our research combines insights from photonic band structure and design, heat diffusion, and optical microscopy to engineer new classes of 2D periodic metamaterials that are optimized for converting light into actively tunable heat and temperature distributions with desired spatial profiles. Synergistic effort and continuous feedback between theory and experiment accelerate the manufacturing of such materials and expand our understanding of their genome, significantly impacting future technologies that depend on nanoscale to micron-scale control over heat sources. The importance of our research lies in the rational, computational design of diffractively coupled metallic nanoparticle lattices can be used to create metasurfaces with actively controllable thermal gradients that can be fully manipulated by optical means despite the effects of heat diffusion. The control of heat flow across such distances through the wavelength/wavevector selective excitation of surface lattice resonance (SLR) modes opens the possibility of using plasmonic array substrates as heat sources for many applications, and for physical and chemical transformation such as phase transitions and chemical reactions/catalysis. Moreover, our work produces meaningful feedback between theoretical design principles and experimental validation, allowing iterative optimization of materials properties and improved understanding of experimental results.

Technical Progress

Over the past year, we have: (1) Theoretically investigated the effects of variable irradiation beam waist upon the excitation of the emergent surface lattice resonances (SLRs) of 2D plasmonic arrays, and its impact on mapping SLR energy-momentum dispersion; (2) Numerically implemented our theory, allowing for the calculation of SLR absorption responses from arbitrary 2D periodic nanoparticle arrays under varying spatial profiles of the illumination source; (3) Demonstrated that k-space hyperspectral imaging is capable of monitoring surface lattice

resonances to understand the dependence of the lattice mode energy on the incident and scattered wavevectors; (4) Investigated the photothermal mechanism of DNA melting to understand why differences in sequence and environment lead to different extracted temperatures as a function of laser intensity; (5) Demonstrated a surface cleaning strategy to remove DNA from substrate-supported metal nanoparticles, allowing samples prepared by electron beam lithography to be reused for multiple experiments; (6) Implemented a wavefront imaging camera (Phasics) to detect wavefront distortions based on local refractive index changes; and (7) Quantified the absorption and scattering linewidth of single nanorods in conjunction with our theoretical models to understand the radiative and nonradiative properties of potential lattice unit cell elements.

Future Plans

We now have in place several crucial components to establish temperature profiles of plasmonic lattices. Specifically, we are able to fabricate arrays using electron-beam lithography and characterize the surface lattice resonances using Fourier space spectroscopy. We have also established a protocol to clean and therefore reuse the same samples after DNA nanothermometry, while understanding any outstanding differences between expected/simulated and experimental temperatures using this super-resolution technique. Finally, our wide-field photothermal imaging based on wavefront sensing is now working. Establishing all these components first has been crucial for investigating plasmonic lattices and is a major departure from temperature imaging of small coupled nanoparticle assemblies (dimers and trimers). We therefore plan to now combine our expertise and investigate theoretically designed plasmonic lattices for unique temperature profiles depending on lattice spacings as well as unit cell structure. In particular, we will measure diffraction-limited temperatures across large distances using a phase imaging camera. We will compare these temperature to those obtained at the sub-diffraction-limited level using the DNA nanothermometry tools. Throughout, theoretical predictions will be used to guide our choice of excitation wavelength, polarization, and angle of incidence to manipulate the thermal profiles within the arrays, with the ultimate goal to actively control temperature both at the mesoscale, covering the entire lattice, as well as nanoscale by resolving the individual unit cells.

Broader Impacts and Workforce Development

Because our research involves three groups at different universities, DMREF students gain valuable experience in collaboration, which is a key component for successful careers in STEM disciplines. The project has trained undergraduates, graduate students, and postdoctoral researchers in an array of disciplines including materials science, physical chemistry, physics, and nanotechnology. Additionally, by leveraging programs such as NSF REU, RET, and LSAMP, as well as several regional outreach programs that promote STEM literacy at the K-12 level, our DMREF program is not only upskilling and supporting the existing workforce but also growing the workforce for the next generation of scientists and engineers.

Data Management and Open Access

All DMREF related computer codes used to calculate the photothermal responses of individual plasmonic nanoparticles and arrays of plasmonic nanoparticles are freely available from our team website (https://faculty.washington.edu/masiello/dmref/). All relevant data needed to reproduce work from our publications is also made available at the same team website.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The ability to control temperature at both nanoscale (<100 nm) and micron-scale (~1-1000 μm) dimensions has important implications for a host of applications including heat-assisted magnetic recording for improved data storage, photothermal therapy for targeted treatment of disease, thermal stimulation of cellular processes, thermal encoding of encrypted data, and local control of thermally-initiated chemical transformations. Plasmonic nanomaterials have emerged as a promising candidate for these applications, due to their ability to transduce far-field electromagnetic radiation into sub-diffraction-limited sources of heat via the non-radiative decay of localized surface plasmons. However, one challenge with these materials is thermal diffusion, in which heat, even when applied to a localized region of space, has the tendency to spread out and produce a temperature change that is spatially uniform throughout a material. This thermal diffusion severely limits the degree of spatial correlation between the heat power supplied via plasmon excitation and the temperature change that it induces, making it difficult to control the temperature profile of a material with the nanoscale precision needed to realize many of the applications cited above. Our unified predict-make-measure workflow has drastically accelerated the design of thermal metamaterials composed of 2D periodic plasmon lattices that are capable of localizing thermal gradients that are actively controllable using free space light of varying frequency, polarization, and wave vector.

Publications and References

1. X. G. Juarez, F. Freire-Fernández, S. Khorasani, M. R. Bourgeois, Y. Wang, D. J. Masiello, G. C. Schatz, T. W. Odom, *Chiral Optical Properties of Plasmonic Kagome Lattices*, ACS Photonics, **11**, 673-681 (2024). DOI: 10.1021/acsphotonics.3c01518
2. C. A. West, S. A. Lee, J. Shooter, E. K. Searles, H. J. Goldwyn, K. A. Willets, S. Link, D. J. Masiello, *Nonlinear effects in single-particle photothermal imaging,* Journal of Chemical Physics*,* **158**, 10370 (2023). DOI: 10.1063/5.0132167
3. M. R. Bourgeois, A. W. Rossi, S. Khorasani, D. J. Masiello, *Optical Control Over Thermal Distributions in Topologically Trivial and Non-Trivial Plasmon Lattices*, ACS Photonics, **9**, 3656–3667 (2022). DOI: 10.1021/acsphotonics.2c01155
4. T. Zuo, H. J. Goldwyn, D. J. Masiello, J. S. Biteen, *Model-Based Insight into Single-Molecule Plasmonic Mislocalization*, Journal of Physical Chemistry C, **125**, 24531-24539 (2021). DOI: 10.1021/acs.jpcc.1c07989
5. P. A. Reinhardt, A. P. Crawford, C. A. West, G. DeLong, S. Link, D. J. Masiello, K. A. Willets, *Toward Quantitative Nanothermometry Using Single-Molecule Counting*, Journal of Physical Chemistry B, **125**, 12197-12205 (2021). DOI: 10.1021/acs.jpcb.1c08348

Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM): An NSF Materials Innovation Platform

Materials Innovation Platform: PARADIM DMR-2039380
MIP Director: Darrell G. Schlom, Department of Materials Science and Engineering, Cornell University, schlom@cornell.edu.
MIP Co-Director (or Associate Director): Tyrel M. McQueen, Departments of Chemistry/Physics and Astronomy/Materials Science and Engineering, Johns Hopkins University, mcqueen@jhu.edu.
MGI PI Meeting Participant in 2024: Tyrel M. McQueen, Departments of Chemistry/Physics and Astronomy/Materials Science and Engineering, Johns Hopkins University, mcqueen@jhu.edu
Participating Institutions: Cornell University, Johns Hopkins University
Source of Support: NSF-DMR.
Website: **https://paradim.org**.
Keywords: Electronic materials, interface materials, quantum materials, materials-by-design, quantum fabrics.

Project Scope

Creating new interface materials with unprecedented properties, by design rather than by serendipity, is accomplished in PARADIM through a synergistic set of user facilities dedicated to theory (figuring out where to put the atoms for useful behavior), synthesis (putting the atoms in the targeted positions), and characterization (seeing that the atoms are indeed in the desired positions). Each of these world-class user facilities is equipped with the latest tools, techniques, and expertise to realize this materials-by-design dream. Users from throughout the nation are using PARADIM to discover and create interface materials for the next generation of electronics and optoelectronics. These new materials are enabling novel ways for electrons to carry information in solid-state devices and efficiently interact with magnetic, electrical, and optical stimuli.

Relevance to MGI

PARADIM's vision is to democratize materials discovery in the U.S.A. and to enable a more effective way of pursuing materials research, one that accelerates materials discovery by establishing a materials discovery ecosystem—a national community of practitioners—and equipping them with theoretical and experimental methods that enable them to reduce to practice the inorganic materials of which they dream. Discovering electronic materials—by design rather than by serendipity—is accomplished through a synergistic set of state-of-the-art facilities dedicated to theory, synthesis, and characterization. PARADIM's bulk crystal growth facility at Johns Hopkins is the only location within the United States where all major optical floating-zone techniques are available at a single site, including the only location in the world where floating zone growths in supercritical fluids are possible. In PARADIM's thin film facility users can select between a record 62 elements to synthesize the materials they envision by MBE, with integrated ARPES for precise electronic structure determination in quantum fabrics. PARADIM's electron microscopy facility has enabled the highest spatial resolution scanning tunneling electron microscopy (0.39 Å) ever achieved on 2D materials, and is continuing to push the frontier with advanced pixel array detectors and state of the art data analysis techniques. PARADIM's theory facility draws on expertise and computing capabilities across institutions to provide ground-breaking computational models and predictions, including through the PARADIM-developed tool specifically for interface materials: Mismatched INterface Theory (MINT). All PARADIM facilities electronically capture as much data as possible and is developing the big-data tools and techniques to extract insights from these data in real-time. PARADIM's in-house research team leverages these facilities to develop quantum fabrics for the next generation of electronics.

Technical Progress

During its eight years of operation, PARADIM has made several key accomplishments. Research enabled by the Platform led to a total of 291 peer-reviewed journal publications—including in *Nature*, *Science*, and *Science Advances*. Among all PARADIM works several have been recognized by Web of Science as highly cited papers: 9 publications acknowledging PARADIM, plus 3 additional papers acknowledging use of the Helios FIB, for which PARADIM was the largest contributor beyond the funds coming from Cornell University. External users' work led to 80 publications in peer-reviewed journals and 45 publications report local users' research.

Exciting discoveries made by PARADIM users include: (i) a new material that is free of rare-earth elements yet has the highest magnetostrictive coefficient ever achieved at room temperature (10x higher than bulk FeGa and nearly twice as high as Terfenol-D); (ii) the most efficient transverse thermoelectric ever discovered, with performance comparable to commercial longitudinal thermoelectrics, but with drastically reduced energy loss at the contacts; (iii) a new layered nickelate superconductor—predicted by theory and experimentally realized; (iv) the first example of using biaxial strain to transmute a normal metal into a superconductor; (v) a method to peel single-crystal oxide films off their substrates to permit wafer-scale interfacing between high-quality films of virtually any complex oxide, free of epitaxial constraints; (vi) Reduction to practice of a new theoretical prediction—utilizing colinear antiferromagnetic metals with low symmetry, rather than spin-orbit coupling—to achieve efficient spin-transfer torque switching; (vii) synthesis of a visible-light photocathode with unusually high efficiency (quantum efficiencies exceeding 2% at 532 nm) at film thicknesses as low as 4 nm. These epitaxial Cs_3Sb films have an order of magnitude higher quantum efficiency at 650 nm than polycrystalline Cs_3Sb films.

Future Plans

PARADIM will continue to update and enhance its world unique capabilities in synthesis, characterization, and theory to accelerate materials by design, and provide a nexus for the discovery and use of interfacial quantum materials, and hopes to expand towards activities that help bridge the "valley of death" between a material discovery and its translation to devices that improve society.

Broader Impacts and Workforce Development

Since its inception PARADIM has run 17 Summer Schools in various formats: purely remote, hybrid, and in-person, for a total of over 400 selected participants. In recent years, thanks to webinar capabilities, all lectures were live streamed to the web and reached a wide audience. All recorded materials including from past years are available as part of PARADIM's Materials-by-Design Toolbox (https://www.paradim.org/toolbox) to inform potential users about relevant capabilities available through PARADIM user facilities. Thanks to the grant *REU-Site: Summer Research at PARADIM*, DMR-2150446, PARADIM continues to offer REU programming at Cornell and Johns Hopkins for a total of 14 participants annually, who developed new protocols and systems to improve the MIP-experience for future users of PARADIM. The program concludes with an in-person convocation at Cornell University with all participants (including from JHU) and many of the mentors. In addition, PARADIM together with all other members of the family of MIPs, co-organized or participated in several *NSF-DMR Materials Innovation Platform Forums* held at MRS Fall Meetings and the ACS Meeting, where current Platforms presented their capabilities, users shared their success stories and various flash talks highlighted the breadth of research pursued at DMR MIPs.

Data Management and Knowledge Sharing

All PARADIM facilities are open to all users via a proposal process, facilitating the use of world-unique capabilities by a broad range of scientists. In addition, significant material products from PARDAIM successes will be produced in bulk by REU interns and made available to other researchers via a proposal process. All data from PARADIM facilities is recorded and stored for future use. After a period of inactivity or completion of scientific publications by the primary users, all data associated with user projects is made publicly available.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Multiple commercial entities currently utilize PARADIM facilities for research directly related to commercialization and the entry into new markets. This is in addition to efforts designed to enhance the deployment of intellectual property (IP) being generated by the in-house research team.

Publications and References

1. C.T. Parzyck, V. Anil, Y. Wu, B.H. Goodge, M. Roddy, L.F. Kourkoutis, D.G. Schlom, and K.M. Shen, "Synthesis of Thin Film Infinite-Layer Nickelates by Atomic Hydrogen Reduction: Clarifying the Role of the Capping Layer," *APL Mater.* **12**, 031132 (2024).
2. C.T. Parzyck, N.K. Gupta, Y. Wu, V. Anil, L. Bhatt, M. Bouliane, R. Gong, B.Z. Gregory, A. Luo, R. Sutarto, F. He, Y.-D. Chuang, T. Zhou, G. Herranz, L.F. Kourkoutis, A. Singer, D.G. Schlom, D.G. Hawthorn, and K.M. Shen, "Absence of $3a_0$ Charge Density Wave Order in the Infinite-Layer Nickelates $NdNiO_2$," *Nat. Mater.* **23**, 486–491 (2024).
3. C.A. Mizzi, S.K. Kushwaha, P.F.S. Rosa, W.A. Phelan, D.C. Arellano, L.A. Pressley, T.M. McQueen, M.K. Chan, and N. Harrison, "The Reverse Quantum Limit and its Implications for Unconventional Quantum Oscillations in YbB_{12}," *Nat. Commun.* **15**, 1607 (2024).
4. N.J. Schreiber, L. Miao, B.H. Goodge, L.F. Kourkoutis, K.M. Shen and D.G. Schlom, "A Model Heterostructure with Engineered Berry Curvature," *APL Mater.* **11**, 061117 (2023).
5. Z. Shao, N. Schnitzer, J. Ruf, O.Y. Gorobtsov, C. Dai, B.H. Goodge, T. Yang, H. Nair, V.A. Stoica, J.W. Freeland, J. Ruff, L.-Q. Chen, D.G. Schlom, K.M. Shen, L.F. Kourkoutis, and A. Singer, "Real-Space Imaging of Periodic Nanotextures in Thin Films via Phasing of Diffraction Data," *Proc. Natl. Acad. Sci. U.S.A.* **120**, e2303312120 (2023).
6. J.L. Hart, L. Bhatt, Y. Zhu, M.-G. Han, E. Bianco, S. Li, D.J. Hynek, J.A. Schneeloch, Y. Tao, D. Louca, P. Guo, Y. Zhu, F. Jornada, E.J. Reed, L.F. Kourkoutis, and J.J. Cha, "Emergent Layer Stacking Arrangements in *c*-Axis Confined $MoTe_2$," *Nat. Commun.* **14**, 4803 (2023).
7. X. Bai, S.-S. Zhang, H. Zhang, Z. Dun, W.A. Phelan, V.O. Garlea, M. Mourigal, and C.D. Batista, "Instabilities of Heavy Magnons in an Anisotropic Magnet," *Nat. Commun.* **14**, 4199 (2023).
8. K.G. Koster, Z. Deng, C.E. Moore, J.P. Heremans, W. Windl, and J.E. Goldberger, "Axis-Dependent Conduction Polarity in WSi_2 Single Crystals," *Chem. Mater.* **35**, 4228-4234 (2023).
9. Y. Tarn, M. Sinha, C. Pasco, D.G. Schlom, T.M. McQueen, K.M. Shen, and B.D. Faeth, "An Algorithm for Subtraction of Doublet Emission Lines in Angle-Resolved Photoemission Spectroscopy," *J. Electron. Spectrosc. Relat. Phenom.* **265**, 147323 (2023).
10. A. Gupta, A. Weiser, L. Pressley, Y. Luo, C. Lygouras, J. Trowbridge, W.A. Phelan, C.L. Broholm, T.M. McQueen, and W.K. Park, "Topological Surface States in the Kondo Insulator YbB_{12} Revealed via Planar Tunneling Spectroscopy," *Phys. Rev. B* **107**, 165132 (2023).
11. M.T. Kiani, Q.P. Sam, G. Jin, B. Pamuk, H.J. Han, J.L. Hart, J.R. Stauff, and J.J. Cha, "Nanomolding of Metastable Mo_4P_3," *Matter* **6**, P1894-1902 (2023).
12. K. Azizie, F.V.E. Hensling, C.A. Gorsak, Y. Kim, D.M. Dryden, M.K.I. Senevirathna, S. Coye, S.-L. Shang, J. Steele, P. Vogt, N.A. Parker, Y.A. Birkhölzer, J.P. McCandless, D. Jena, H.G. Xing, Z.-K. Liu, M.D. Williams, A.J. Green, K. Chabak, A.T. Neal, S. Mou, M.O. Thompson, H.P. Nair, and D.G. Schlom, "Silicon-Doped β-Ga_2O_3 Films Grown at 1 μm/h by Suboxide Molecular-Beam Epitaxy," *APL Mater.* **11**, 041102 (2023).
13. L.C. Brinson, L.M. Bartolo, B. Blaiszik, D. Elbert, I. Foster, A. Strachan, and P.W. Voorhees, "Community Action on FAIR Data will Fuel a Revolution in Materials Research," *MRS Bulletin* (2023).
14. D.F. Segedin, B.H. Goodge, G.A. Pan, Q. Song, H. LaBollita, M.-C. Jung, H. El-Sherif, S. Doyle, A. Turkiewicz, N.K. Taylor, J.A. Mason, A.T. N'Diaye, H. Paik, I. El Baggari, A.S. Botana, L.F. Kourkoutis, C.M. Brooks, and J.A. Mundy, "Limits to the Strain Engineering of Layered Square-Planar Nickelate Thin Films," *Nat. Commun.* **14**, 1468 (2023).
15. W. Zhao, B. Shen, Z. Tao, Z. Han, K. Kang, K. Watanabe, T. Taniguchi, K.F. Mak, and J. Shan, "Gate-Tunable Heavy Fermions in a Moiré Kondo Lattice," *Nature* **616**, 61–65 (2023).
16. M. Eminizer, S. Tabrisky, A. Sharifzadeh, C. DiMarco, J.M. Diamond, K.T. Ramesh, T.C. Hufnagel, T.M. McQueen, and D. Elbert, "OpenMSIStream: A Python package for Facilitating Integration of Streaming Data in diverse Laboratory Environments," *J. of Open Source Softw.* **8**, 4896 (2023).
17. T. Schwaigert, S. Salmani-Razaie, M.R. Barone, H. Paik, E. Ray, M.D. Williams, D.A. Muller, D.G. Schlom, and K. Ahadi, "Molecular Beam Epitaxy of $KTaO_3$," *J. Vac. Science & Technol. A* **41**, 022703 (2023).
18. Q. Song, S. Doyle, G.A. Pan, I. El Baggari, D.F. Segedin, D. Córdova Carrizales, J. Nordlander, C. Tzschaschel, J.R. Ehrets, Z. Hasan, H. El-Sherif, J. Krishna, C. Hanson, H. LaBollita, A. Bostwick, C. Jozwiak, E. Rotenberg, S.-Y. Xu, A. Lanzara, A.T. N'Diaye, C.A. Heikes, Y. Liu, H. Paik, C.M. Brooks, B. Pamuk, J.T. Heron, P. Shafer, W.D. Ratcliff, A.S. Botana, L. Moreschini, and J.A. Mundy, "Antiferromagnetic Metal Phase in an Electron-Doped Rare-Earth Nickelate," *Nat. Phys.* **19**, 522–528 (2023).
19. L. Caretta, Y.-T. Shao, J. Yu, A.B. Mei, B.F. Grosso, C. Dai, P. Behera, D. Lee, M. McCarter, E. Parsonnet, Harikrishnan K.P., F. Xue, X. Guo, E.S. Barnard, S. Ganschow, Z. Hong, A. Raja, L.W. Martin, L.-Q. Chen, M. Fiebig, K. Lai, N.A. Spaldin, D.A. Muller, D.G. Schlom, and R. Ramesh, "Non-Volatile Electric-Field Control of Inversion Symmetry," *Nat. Mater.* **22**, 207–215 (2023).
20. L.A. Pressley, D. Edey, R. Hanna, S. Chae, J.T. Heron, M.A. Khan, and T.M. McQueen, "Informing Quantum Materials Discovery and Synthesis using X-ray Micro-Computed Tomography," *npj Quantum Mater.* **7**, 121 (2022).

Quasi-Direct Semiconductors

Lead Investigator: José Menéndez, jose.menendez@asu.edu
Participating Institutions: Arizona State University and University of Texas, Austin
Source of Support: NSF-DMREF
Website: None
Keywords: Semiconductors, absorption, indirect, direct, divergence

Project Scope

Quasi-direct semiconductors are indirect-gap materials with a direct transition slightly above the fundamental gap. In the conventional theory of indirect optical absorption, the direct transition appears as an intermediate state, and therefore the predicted absorption strength *diverges* when the photon energy reaches the direct transition. This project's goals are to develop a theoretical framework that eliminates such unphysical divergences, to introduce new approaches to measure absorption coefficients that change by orders of magnitude over the critical spectral range, and to synthesize new quasi-direct materials that provide an additional test of the theoretical and experimental advances.

Relevance to MGI

This project was born as an experimental and theoretical team came together to address the lack of a satisfactory theoretical framework to model optical absorption and emission in quasi-direct semiconductors, including materials as basic and technologically important as germanium. The idea was to start by developing such theory, to devise additional experimental methods to measure optical absorption over the critical spectral range, and to introduce improvements in an iterative fashion that will eventually make it possible to fit experimental data with methods based on a consistent theory. A parallel effort, which exploits synergistically the predictive capabilities of *ab initio* theory and the synthetic know-how of the experimental group, is the growth of new quasi-direct semiconductors for further test of the new optical theory.

Fundamental progress has already been made in developing a theory that eliminates the divergencies of the traditional theory[1] and in developing advanced methods[2] to accurately fit diode responsivities as a way to extract the absorption coefficient as it changes by orders of magnitude between the indirect and direct gap.

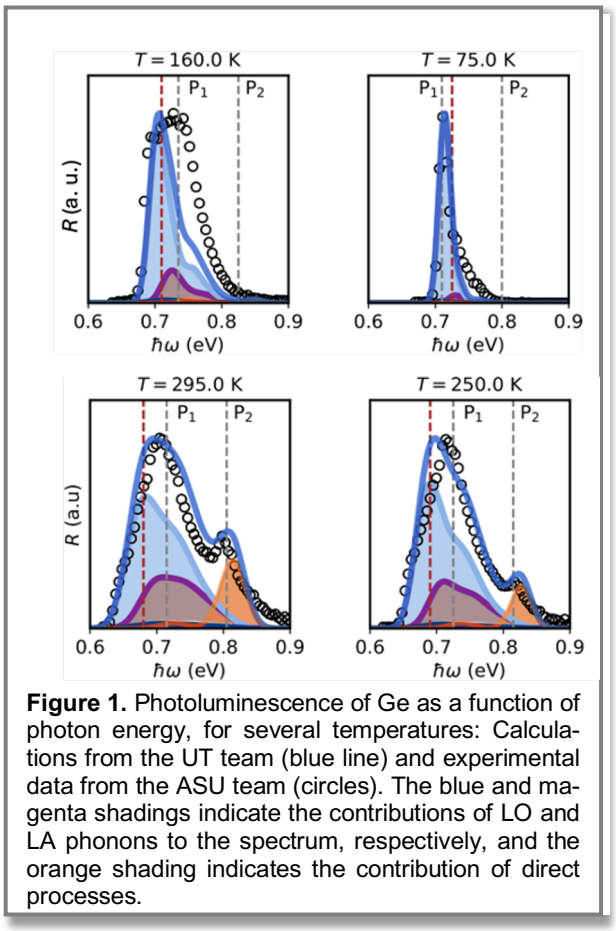


Figure 1. Photoluminescence of Ge as a function of photon energy, for several temperatures: Calculations from the UT team (blue line) and experimental data from the ASU team (circles). The blue and magenta shadings indicate the contributions of LO and LA phonons to the spectrum, respectively, and the orange shading indicates the contribution of direct processes.

Technical Progress

At UT Austin a novel many-body theory of optical absorption and emission was finalized which includes both direct and indirect phonon-assisted transitions on the same footing.[1] Instead of using the standard second-order perturbation theory approach, which leads to infinite indirect absorption at the resonant condition when the photon energy equals the direct gap energy, quasi-degenerate perturbation theory was applied to the degenerate manifolds of electron-hole pairs and electron-hole-phonon triples connected to the ground state by the electric dipole Hamiltonian. As shown in Fig 1, this theoretical approach can—for the first time— explain the temperature dependence of the Ge photoluminescence previously measured at ASU.

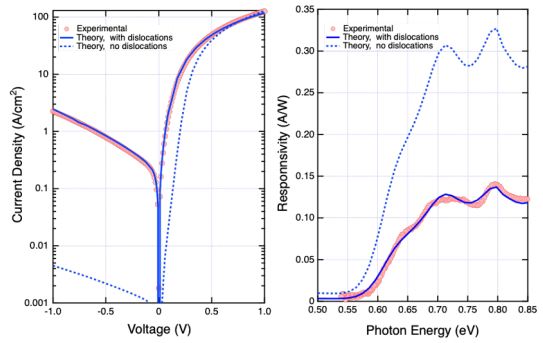


Figure 2. The left panel shows the current-voltage curve and the right panel the optical responsivity of a GeSn pin diode. The dotted blue lines show the predicted results for an ideal diode with no defects, whereas the solid blue line is a *simultaneous* theoretical fit of both curves incorporating dislocation-related and surface recombination traps. The simulation code runs on a standard PC and will be made available to all interested parties. To the best of our knowledge, this is the first time that both the I-V and responsivity curves are fit simultaneously. This opens the door to devising rational approaches to the improvement of optical devices based on the simulation of their basic properties. It is likely to have a broad impact well beyond the specific objectives of this DMREF project.

Measuring the transition from pre-resonant to resonant conditions is critical for a stringent test of the new theory but difficult to carry out in practice because the absorption changes by orders of magnitude. One possible approach is to measure the optical responsivity of diode devices, but this requires a quantitative approach to extract the absorption coefficient from such measurements. We have succeeded in developing such an approach, as demonstrated in Fig. 2 with results from a GeSn diode grown and fabricated at ASU.

Future Plans

The next iteration of our work will be to develop versions of our codes that are numerically simplified to the point that can be routinely used by experimentalists to fit spectra, yet incorporate additional phenomena such as excitonic effects and empirical band parameters that enable such fits. On the experimental side, in addition to the responsivity method explained in Fig. 2, we will use traditional transmittance/reflectance measurements as the most accurate way to extract the absorption coefficient of a material. Since measuring the entire indirect-direct gap range requires ranges of thicknesses that are not compatible with mechanical stability, we will grow epitaxial layers of the interesting materials.

We also plan to advance on the growth of quasi-direct materials not derived from Ge, such as for example SiS. This material will be pursued using the CVD precursor $S(SiH_3)_2$, which we used previously for S-doping of Si.

Broader Impacts and Workforce Development

This project supported the training of a postdoctoral researcher at UT and three graduate students at ASU. The Texas post-doc (Dr. Sabyasachi Tiwari) joined the EPW development team and has been elected a member of its steering committee. Two of the ASU graduate students (Dhruve Ringwala, and Aixin Zhang) have chemistry background and focus on synthesis and structural characterization, while the third student (Matthew Mircovich) has a physics background and focuses on devices and optical properties.

Data Management and Open Access

The methods and software developed at UT Austin are being made available to the community via the v5.8 release of the EPW code and as a core module of the hugely popular Quantum ESPRESSO materials simulation suite. The EPW code (https://epw-code.org) is developed under continuous integration on the GitLab portal, and distributed under the GNU GPL open-source software license. The UT Austin team organized a computational Summer school at UT Austin, which gathered 130 in-person participants and 500 Zoom participants. During this event, Dr Tiwari demonstrated the use of the new quasi-direct perturbation theory module. The PDF files of this demo and the YouTube videos of his lectures are publicly available at https://epw2024.oden.utexas.edu/. A preliminary version of the simulation code of for the optical properties of group-IV material diodes is also available to the public from ASU, and a formal release will be made once the optical module is added.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The project represents an important step towards the full quantitative understanding of the optical properties of semiconductors. It will assist the discovery of new materials by improving the accuracy with which their optical properties can be predicted, and it will open up completely new perspectives for studies of the temperature dependence of those optical properties. The release of the theoretical methods to the public domain has already been started and will also impact areas not directly related to the project, such as the optimization and design of optoelectronic devices.

Publications and References

1. S. Tiwari, E. Kioupakis, J. Menendez, F. Giustino, Unified theory of optical absorption and luminescence including both direct and phonon-assisted processes, Physical Review B 109, 195127 (2024). DOI: 10.1103/PhysRevB.109.195127
2. M.A. Mircovich, J. Kouvetakis, J. Menéndez, A practical theoretical model for Ge-like epitaxial diodes: I. The I–V characteristics, Journal of Applied Physics 135, 124501(2024). DOI: 10.1063/5.0185557
3. C. Emminger, N.S. Samarasingha, M. Rivero Arias, F. Abadizaman, J. Menéndez, S. Zollner, Excitonic effects at the temperature-dependent direct bandgap of Ge, Journal of Applied Physics 131, 165701 (2022). DOI: 10.1063/5.0080158
4. A. Zhang, M.A. Mircovich, D.A. Ringwala, C.D. Poweleit, M.A. Roldan, J. Menéndez, J. Kouvetakis, Ultra-low temperature synthesis of Ge-based optical materials and devices on Si using GeH_3Cl, Journal of Materials Chemistry C 10, 13107 (2022) DOI: 10.1039/d2tc02862j
5. C. Xu, T. Hu, A. Zhang, D.A. Ringwala, J. Menéndez, J. Kouvetakis, *Synthesis of short-wave infrared $Ge_{1-y}Sn_y$ semiconductors directly on Si(100) via ultralow temperature molecular routes for monolithic integration applications*, Journal of Vacuum Science & Technology A **40** 063405 (2022). DOI: 10.1116/6.0002052
6. J. Menéndez, C. Xu, J. Kouvetakis, *Consistent optical and electrical determination of carrier concentrations for the accurate modeling of the transport properties of n-type Ge*, Materials Science in Semiconductor Processing **164** 107596 (2023). DOI: 10.1016/j.mssp.2023.107596
7. M. Zacharias, G. Volonakis, F. Giustino, J. Even, *Anharmonic electron-phonon coupling in ultrasoft and locally disordered perovskites*, npj Computational Materials **9** 153 (2023). DOI: 10.1038/s41524-023-01089-2
8. H. Lee, S. Poncé, K. Bushick, S. Hajinazar, J. Lafuente-Bartolome, J. Leveillee, C. Lian, J.-M. Lihm, F. Macheda, H. Mori, H. Paudyal, W.H. Sio, S. Tiwari, M. Zacharias, X. Zhang, N. Bonini, E. Kioupakis, E.R. Margine, F. Giustino, *Electron–phonon physics from first principles using the EPW code*, npj Computational Materials **9** 156 (2023). DOI: 10.1038/s41524-023-01107-3
9. H. Lee, Y. Zhou, S. Jung, H. Li, Z. Cheng, J. He, J. Chen, P. Sokalski, A. Dolocan, R. Gearba-Dolocan, K.C. Matthews, F. Giustino, J. Zhou, L. Shi, *High-Pressure Synthesis and Thermal Conductivity of Semimetallic θ-Tantalum Nitride*, Advanced Functional Materials **33**, 2212957 (2023). DOI: 10.1002/adfm.202212957
10. M. Zacharias, G. Volonakis, F. Giustino, J. Even, *Anharmonic electron-phonon coupling in ultrasoft and locally disordered perovskites, npj Computational Materials* **9**, 153 (2023). DOI: 10.1038/s41524-023-01089-2
11. M. Zacharias, G. Volonakis, F. Giustino, J. Even, *Anharmonic lattice dynamics via the special displacement method*, Physical Review B 108, 035155 (2023). DOI: 10.1103/PhysRevB.108.035155

Monolayer III-Nitrides and Extreme Quantum Dots

Lead Investigator: Zetian Mi, ztmi@umich.edu
Participating Institutions: University of Michigan, Ann Arbor
Source of Support: NSF-DMREF, AFRL
Website: none
Keywords: GaN, two-dimensional semiconductor, quantum dot, exciton, molecular beam epitaxy

Project Scope

This project will create a new family of nano-quantum materials (nQMs), including two-dimensional (2D) III-nitrides and extreme quantum dots (XQD). Our team predicted that the Coulomb interaction in 2D III-nitrides is so strong it binds electrons and holes into excitons with a binding energy exceeding 1 eV. We will establish an nQM platform with unique quantum functionalities by using the most accurate quantum theory to design the quantum optoelectronic properties of nQMs. Our breakthroughs will transform conventional low-efficiency AlGaN into high-brightness deep ultraviolet (UV) emitters and establish the first controllably interacting semiconductor qubit platform for quantum information science application.

Relevance to MGI

We propose a focused theory-epitaxy-characterization-quantum optoelectronics collaboration. We are developing a systematic quantum theory that integrates three first-principles methods, including Density-Functional Theory, Many-Body Perturbation Theory, and Quantum-Dynamic Cluster Expansion, to precisely predict and determine the electronic, optical, excitonic, and entanglement properties of 2D III-nitrides and XQDs. Atomically thin III-nitrides and XQDs with superior quality are being realized by combining ultrahigh temperature molecular beam epitaxy and selective area growth with polarization, surface, polarity, and quantum engineering. The presence of disorder and spectral diffusion, deleterious effects that plague conventional QDs, are addressed by i) deterministically growing and positioning XQDs on hBN whose atomically smooth surface eliminates interface interdiffusion and disorder, and ii) creating interface excitons with well-aligned dipole and with identical emission that is largely determined by the band alignment of AlN/hBN. We combine time-resolved deep-UV photoluminescence spectroscopy and differential transmission spectroscopy to demonstrate controllable XQD–XQD coupling and controlled formation of direct and indirect excitons, biexcitons, and dropletons at room temperature. The potential of the nQMs platform is realized by taking key steps toward extraordinary quantum optoelectronic devices, including deep UV light emitters, entanglement detectors, and coupled XQD systems.

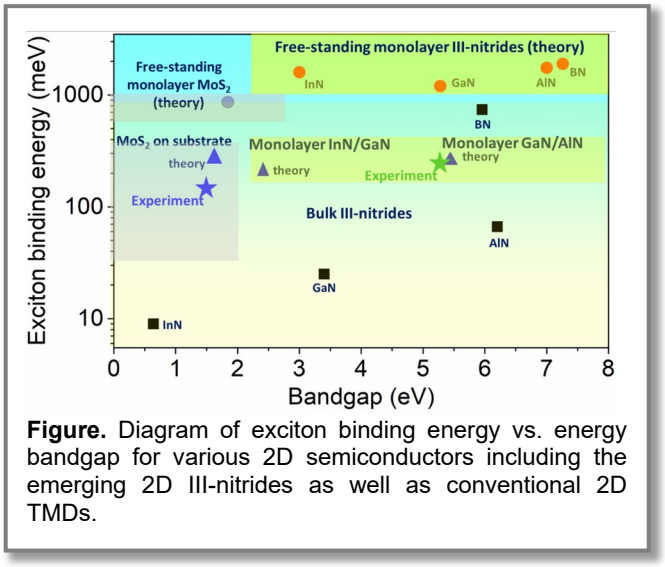


Figure. Diagram of exciton binding energy vs. energy bandgap for various 2D semiconductors including the emerging 2D III-nitrides as well as conventional 2D TMDs.

Technical Progress

This project has four Thrusts, including Thrust 1 – Quantum Theory and Design, Thrust 2 – Epitaxy of III-Nitride Monolayers and Extreme Quantum Dots, Thrust 3 – Optical Spectroscopy, and Thrust 4 – Quantum Optoelectronics. Quantum theory and design. As a key theory challenge, one needs to connect interaction chains to actual semiconductor quantum-system performance. This means developing a detailed and systematic analysis of quantum-dynamic processes that are mediated by multi-electron–photon–phonon interactions. Our focus has been exploring such interactions in nQM semiconductors, related to their nonlinear prosperities. Specifically, we have compared atomically thin CrSBr monolayer with bulk to explore exciton lifetime. We also have explored the complementary excitonic effects in 2D III-nitrides to quantify how their strong exciton binding can be leveraged to achieve room-temperature quantum. Epitaxy of III-Nitride Monolayers and Extreme Quantum Dots. We have

developed the first method for the epitaxy of pristine, wafer-scale monolayer hBN on graphene. We discover that the in-plane hBN/G interface can be precisely controlled, enabling the scalable epitaxy of unidirectional monolayer hBN on graphene, which exhibits a uniform moiré superlattice consistent with single-domain hBN, aligned to the underlying graphene lattice. Interface engineering in heterostructures at the atomic scale has been a central research focus of nanoscale and quantum material science. Near-perfect quantum interfaces can be readily synthesized on the semipolar plane instead of the conventional c-plane of GaN/AlN heterostructures.

Optical Spectroscopy and Quantum Optoelectronics. We concluded that In clustering in InGaN leads to energy transfer from the high energy states near the center of the a nanostructure to the deeper states on the semipolar facets near the edge via intermediate states. We further studied the effect of geometry on bandgap tunability. Typically, at sub 50 nm dimensions, surface recombination reduces the PL quantum efficiency. However, we observed strong PL, indicating the dominance of excitonic properties.

Future Plans

Our future plans include: i) develop quantum theory and design of InN, GaN, and AlN extreme quantum dots on hBN, 2) study the epitaxy and structural, optical, and excitonic properties of the spontaneous formation of InN, GaN, and AlN extreme quantum dots, and study the two-photon absorption and entanglement detection utilizing these novel quantum nanostructures.

Broader Impacts and Workforce Development

This project will pioneer 2D III-nitride nQMs with quantum optoelectronic properties enabling novel applications ranging from high-efficiency deep UV light emitters to controlled qubit interactions. The broader impacts also include the highly interdisciplinary nature of this project and outreach to undergraduates, underrepresented minorities, and K-12. The education and outreach program includes 1) encouraging underrepresented minorities and women in careers in science and engineering through the appealing potential social impacts of the research, 2) involving undergraduate students in frontier research, and 3) communicating the research to the general public, including the MSHORE REU program at the University of Michigan and the recently established Midwest Quantum Collaboratory to reach out to the broader public.

Data Management and Open Access

During this project, data from quantum theory, design and modeling, epitaxy, structural and optical characterization and analysis, and device processing and measurements will be generated. Data that are of high impact results will be made available to the general public through peer-reviewed journal and conference publications (including supplementary material), seminars, and presentations. More detailed data analysis is also published after the completion of each project, which may take the form of final project reports, master and doctoral thesis, books, and book chapters.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Some IP related to this project has been licensed to NS Nanotech, Inc., which was a spin-off from the University of Michigan with Mi being a co-founder.

Publications and References

1. P. Wang, W. Lee, J.P. Corbett, W.H. Koll, N.M. Vu, D.A. Laleyan, Q. Wen, Y. Wu, A. Pandey, J. Gim, D. Wang, D.Y. Qiu, R. Hovden, M. Kira, J.T. Heron, J.A. Gupta, E. Kioupakis, Z. Mi, "Scalable Synthesis of Monolayer Hexagonal Boron Nitride on Graphene with Giant Bandgap Renormalization", Advanced Materials, 2201387, 2022. 10.1002/adma.202201387
2. Y. Wu, P. Wang, W. Lee, A. Aiello, P. Deotare, T. Norris, P. Bhattacharya, M. Kira, E. Kioupakis, and Z. Mi, "Perspectives and Recent Advances of Two-dimensional III-Nitrides: Material Synthesis and Emerging Device Applications," Appl. Phys. Lett., vol. 122, 160501, 2023. https://doi.org/10.1063/5.0145931
3. D. A. Laleyan, W. Lee, Y. Zhao, Y. Wu, P. Wang, J. Song, E. Kioupakis, and Z. Mi, Epitaxial Hexagonal Boron Nitride with High Quantum Efficiency, APL Materials, vol. 11, 051103, 2023. https://doi.org/10.1063/5.0142242
4. Y Wu, P Zhou, Y Xiao, K Sun, D Wang, P Wang, Z Mi, Achieving atomically ordered GaN/AlN quantum heterostructures: The role of surface polarity, Proceedings of the National Academy of Sciences, vol. 120 (44), e2303473120, 2023. https://doi.org/10.1073/pnas.2303473120
5. Yuanpeng Wu, Xianhe Liu, Ayush Pandey, Peng Zhou, Wan Jae Dong, Ping Wang, Jungwook Min, Parag Deotare, Mackillo Kira, Emmanouil Kioupakis, Zetian Mi, "III-Nitride Nanostructures: Emerging Applications for Micro-LEDs, Ultraviolet Photonics, Quantum Optoelectronics, and Artificial Photosynthesis," Progress in Quantum Electronics, vol. 85, 100401, 2022. https://doi.org/10.1016/j.pquantelec.2022.100401.

GOALI: / DMREF: Multimodal design of revolutionary additive-enabled oxide dispersion strengthened superalloys

Lead Investigator: Michael Mills, mills.108@osu.edu
Participating Institutions: The Ohio State University, University of Michigan, GE Aerospace Research, NASA Glenn Research Center, Air Force Research Laboratory
Source of Support: NSF-DMREF
Website: : https://github.com/mesoOSU
Keywords: High temperature alloys, oxide dispersion strengthening, additive manufacturing.

Project Scope

This project will develop new knowledge and strategies for creating a new class of metallic materials for a wide range of demanding, high temperature applications in aerospace and power generation. We are exploiting a novel additive-processing route for creating oxide dispersion strengthened (ODS) metallic alloys as well as advanced novel machine learning approaches to characterize multiscale microstructure, develop property/processing linkages, and accelerate the iterative design of new additive ODS alloys.

Relevance to MGI

The capability to "directly-write" high-quality, additive ODS alloys is transformational, enabling the full power of the Materials Genome Initiative (MGI) approach to be harnessed (see the **Figure**) to enable the rapid development of ODS alloys. We will extend the NASA additive ODS process for the first time to two-phase γ/ γ' strengthened superalloys. The transformative attributes of this combination will motivate two structural application regimes: *Design Objective 1* – intermediate/high temperatures for extended durations, which is of relevance for aerospace and power generation (and thus our GOALI partner GE Aerospace Research), and *Design Objective 2* – extreme temperature for short duration, which are conditions relevant to hypersonics (and thus our AFRL collaborators).

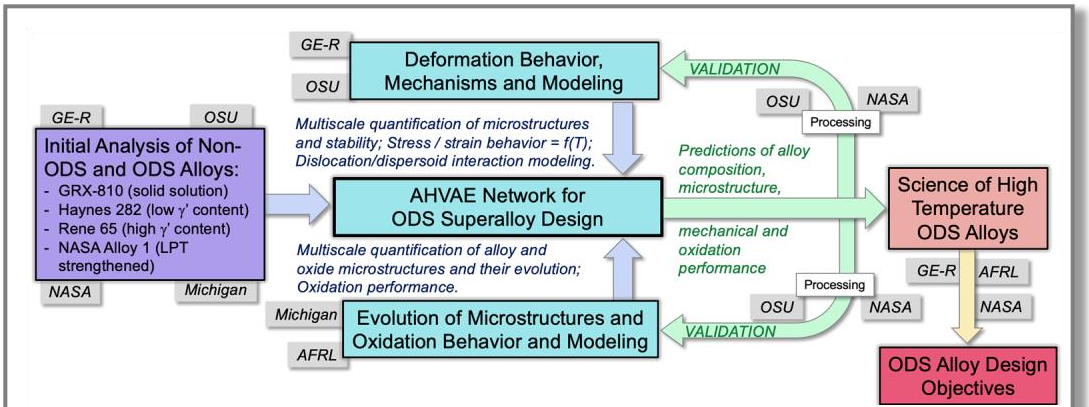


Figure. Overview of DMREF team, the integrated and collaborative approach and workflow, and the proposed roles for participants and partners.

Technical Progress

The additive ODS alloy GRX-810 developed by NASA, in collaboration with the DMREF team, has extraordinary creep strength at 1100°C compared with current commercial superalloys and equiatomic NiCoCr ODS alloy. Multiscale electron microscopy characterization of the as-built and post-creep microstructures has been performed, including grain boundary precipitates, dislocation substructures, and oxide distribution, structure and chemistry. A novel stereomicroscopy technique has been developed to quantify the dislocation density, oxide particle size distribution and volume fraction. Remarkably, the profound strengthening provided by the oxides in GRX-810 occur for a volume fraction of only 0.5%, which is critical feedback for optimizing the oxide coating process of the metal powders. The structure and composition of the oxides are distinctly different when comparing GRX-810 (monoclinic Y_2O_3) and NiCoCr-ODS (cubic Y_2O_3), which may affect the "pinning power" of the oxides. The dislocation substructure evolves after creep at 1073°C more distinctly for NiCoCr ODS, indicating that

recovery (softening) processes are more active than for GRX-810. Static (no applied stress) oxidation studies have been performed at UM to explore the "weight gain" at 1100°C in dry air for additively processed GRX-810 and NiCoCr (both with and without oxides). These studies have already yielded surprising results: GRX-810 with oxides exhibits the most rapid weight gain, while NiCoCr-ODS the slowest. Characterization of the oxidized surface layers will provide insight into the oxides formed at very high temperatures. Further understanding of localized phase transformations (LPT) at deformation stacking faults in γ' superalloys has also continued. The extension of LPT to Co-based alloys is also being studied in collaboration with colleagues at the University of Erlangen. The synergistic effects possible by combining ODS and LPT strengthening will be explored in the next phase of the program.

Future Plans

We will extend additive ODS processing to alloys strengthened by γ' (Haynes 282 and modified LPT alloy) and γ'' (IN 718) precipitates. These alloys are widely employed in industry, but their reinforcement with oxides has never been explored previously. Recrystallization studies for the ODS alloys are in progress using gradient-shaped samples that will enable rapid assessment of strain and temperature combinations to achieve desirable grain structures. Capabilites for mechanical testing of the additive ODS alloys at high temperatures (1100C to melt) have been developed, which will allow for monotonic and transient deformation experiments. New screening tests for gathering high-temperature creep resistance over a range of stresses and temperatures in a single specimen have been developed and demonstrated on surrogate materials. Modeling of dislocation oxide interactions and substructure development in the presence of pinning oxide particles is also underway, as is the deployment of a novel AHVAE Network approach to merging characterization and property data for predication of alloy composition and processing to achieve desired properties (see Figure).

Broader Impacts and Workforce Development

At UM, a masters' student (Eli Rotman) will be graduating soon and George Vukovik is an incoming PhD student starting in August. Two rising junior MSE students (Isabelle Hopf and Trevor Balduck) are quantifying grain growth in the ODS and non-ODS alloys, and are also creating art pieces that are related to their research work. At OSU, Jacob Pellicotte and Britton DeGarmo have been developing advanced mechanical testing methods. Jacob is on target to graduate in December and new PhD student Kojo Benefo will takeover testing. Ananya Kameswari is working with Laura Dial of GE Research on modeling the strain state in gradient cross-section samples for recrystallization studies of GRX-810. Sugham Chattoraj will start as an incoming PhD in August. Prof. Stephen Niezgoda is in the Air Force Summer Faculty Fellowship Program at AFRL during summer of 2024. Prof Calvin M. Stewart ran the MATX summer school a six-week program where high school and undergraduate students in central ohio, gained practical skills in in thermomechanical testing, 3D printing, and modeling/simulation. The summer schoolers participated in a thermomechanical test of GRX 810. Multiple graduate students and post-doctoral research associates participating in the program will be attending the TMS Spring Meeting in 2025.

Data Management and Open Access

Weekly Zoom meetings have brought together the academic team, GE Aerospace Research, AFRL, and NASA staff. Cloud-based file sharing has utilized the OSU OneDrive system. Research codes are being deployed at https://github.com/mesoOSU.

Advancing Along the Materials Development Continuum and Partnerships to Translation

This project is enabling a novel class of alloys that combines additive manufacturing, ODS, and superalloy precipitation. Research activities on individual or two of these approaches exist to date, but this is the first project to combine all three. The applications of advanced modeling, testing, processing and characterization tools will enable efficient and comprehensive understanding of these new materials. Engagement of NASA and GE Aerospace Research as collaborators will enable smooth transition and adoption of the technology to industrialization in the future.

Publications and References

T.M. Smith, C.A. Kantzos, N.A. Zarkevich, B.J. Harder, M. Heczko, P.R. Gradl, A.C. Thompson, M.J. Mills, T.P. Gabb, J. W. Lawson, "3D Printable Alloy Designed for Extreme Environments," Nature, 617, pages 513–518 (2023) https://doi.org/10.1038/s41586-023-05893-0

L Feng, R Shi, CH Zenk, MJ Mills, Y Wang, "Phase Field Modeling of Shearing Processes of a Dual-lobed γ''| γ'| γ'' Coprecipitate," Acta Materialia, 1186932023 (2023), https://doi.org/10.1016/j.actamat.2023.118693

S Mukhopadhyay, F Xue, H Sriram, RW Hayes, EA Marquis, Y Wang, MJ Mills, "Preferential γ′ Precipitation on Coherent Annealing Twin Boundaries in Alloy 718", Proceedings of the 10th International Symposium on Superalloy 718 and Derivatives, TMS 2023. pp. 135-146 (2023), https://doi.org/10.1007/978-3-031-27447-3_9

D Barba, A Egan, S Utada, Y Gong, YT Tang, V Mazanova, MJ Mills, RC Reed, "Deformation Mechanisms Rationalisation to Design for Creep Resistance in Polycrystalline Ni-Based Superalloys," Metallurgical and Materials Transactions A, Volume 54, pp. 1886–1901 (2023), https://doi.org/10.1007/s11661-022-06922-9

AB Parsa, M Sirrenberg, D Bürger, MJ Mills, A Dlouhy, G Eggeler, "Yield stress anomaly and creep of single crystal Ni-base superalloys – Role of particle size," Materials Science and Engineering: A, Volume 899, 146403 (2024) https://doi.org/10.1016/j.msea.2024.146403

Accelerated Data-Driven Discovery of Ion-Conducting Materials

Lead Investigator: Dr. Yifei Mo, yfmo@umd.edu
Participating Institutions: University of Maryland, Northwestern University, Lehigh University
Source of Support: NSF-DMREF
Website: none
Keywords: *ion-conducting materials, high-throughput materials discovery, rapid synthesis, microstructure design*

Project Scope

The objective of this DMREF project is to integrate rapid ceramic synthesis with first-principles data-driven computation, high-throughput measurements, and microstructural modeling to accelerate the discovery of new ceramic oxide materials, using Na-ion conductors as model systems. The project targets developing an integrated framework for designing ion-conducting materials by optimizing composition, microstructure, and sintering conditions. The goal is to produce new Na-ion conducting oxides with optimized compositions and microstructures through the Ultrafast High-temperature Sintering (UHS) method.

Relevance to MGI

This project achieves the MGI objective by tightly integrating experiments, computation, and theory through a closed, iterative feedback loop. Loop 1 (Composition discovery) combines first-principles computation, high-throughput screening, and machine learning to predict new Na-ion conducting compounds. These predictions are validated through rapid synthesis and characterization using UHS, with experimental results feeding back to refine computational models. Loop 2 (Microstructure design) iteratively connects UHS sintering, characterization, and modeling to understand microstructural evolution and develop Time-Temperature-Transformation (TTT) diagrams. Loop 3 unifies composition, microstructure, and synthesis conditions into a comprehensive framework for designing new ion-conducting materials. This collaborative process enhances each component, accelerates discovery, and builds a knowledge base for designing materials with specific properties. The iterative feedback ensures continuous improvement and effective collaboration across synthesis, characterization, and modeling, leading to significant advances in all aspects and faster materials development.

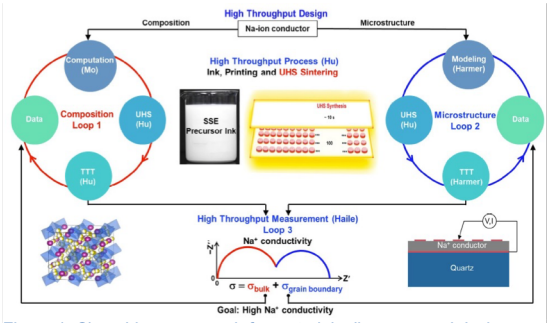


Figure 1. Closed-loop approach for materials discovery and design integrating high-throughput rapid synthesis, measurements, computation, and modeling.

Figure. Closed-loop approach for materials discovery and design integrating high-throughput rapid synthesis, measurements, computation, and modeling.

Technical Progress

Our project has made substantial technical and scientific progress toward accelerating the discovery and development of Na-ion conductors through our iterative close-loop approach of computational studies, experimental validations, and the synthesis of new materials for fast Na-ion conductors. We identified and established the design principles for Na-ion conductors by analyzing the structures of many Na-ion conductors. By applying our design principle in high-throughput computation, we discovered a few dozen novel Na-ion conductors. Many of these newly discovered structures have been examined by our iterative close-loop approach based on the rapid UHS synthesis method. Experimentally, multiple oxides are confirmed with high bulk ionic conductivity of 10^{-4} to 10^{-3} S/cm at room temperature, comparable with current state-of-the-art oxide Na-ion conductors in bulk conductivity. We successfully synthesized this family of $Na_{3x}M_{2-x}Cl_6$-containing (M = La, Ce, Nd, Sm) halide Na^+ conductors with high ionic conductivities of up to 1.4 mS/cm at 25 °C for this series of new Na-ion conductor family, which is the highest reported and is a significant improvement over the previous halide Na-ion conductor Na_2ZrCl_6 (0.02 mS/cm). This discovery of a new chloride Na-SIC family with the highest reported Na ionic conductivity is a strong validation of our design principle for fast Na-ion conductors.

Future Plans

Our iterative close-loop approach will be continued to identify novel materials with fast Na-ion conduction. Using our iterative close-loop approach, the computation predicted materials will be further synthesized and compared with the computation prediction. In addition, more advanced machine learning based approaches are employed to make better predictions of the new materials. Novel iterative close-loop are also being established in both computation and experiments for the wide composition space of the newly identified structures.

Broader Impacts and Workforce Development

The Na-ion conducting materials discovered in this project are pivotal for developing economical, environmentally friendly, and sustainable Na-ion and Na-metal batteries, offering alternatives to Li-ion technology and promoting renewable energy for transportation and grid storage. The project has provided extensive learning opportunities for students at UMD, NU, and Louisiana State University, where characterization techniques and Na-ion conductors are discussed in various courses. Students gain hands-on experience in computational modeling, synthesis, and characterization of ion conductors, fostering the development of future MGI researchers. All PIs leverage their interdisciplinary expertise to create unique educational opportunities for a diverse range of students, including graduate, undergraduate, and K-12 students, with a focus on underrepresented minorities. Our education and outreach efforts emphasize the core MGI components, such as data-driven closed-loop materials design, as essential training for the next-generation workforce in conjunction with the research activities. By integrating MGI philosophy into educational programs and community outreach, we aim to convey the project outcomes and their significance beyond the immediate research community. This approach ensures that the knowledge and benefits of the project are widely disseminated, fostering a well-connected and highly trained materials R&D workforce capable of driving future innovations.

Data Management and Open Access

For the paper published, the data was shared through the publication. The code for the published version of the project is shared through the Github of Mo's group https://github.com/mogroupumd and the data through the publisher website (DOI: 10.1038/s41467-023-43436-3) The current metadata from computation and experiment will be shared through the publication as both public depository and in a queryable database in the future.

Advancing Along the Materials Development Continuum and Partnerships to Translation

R&D of ion-conducting ceramic materials has largely been conducted in a slow, trial-and-error fashion impeded by three challenges: 1) long synthesis and processing times (~10–100 hours), leading to undesired side reactions and volatile elemental loss; 2) a limited number of available compounds that exhibit fast ion-conduction with mechanical and chemical stability; and 3) a lack of understanding and rational control of microstructures during conventional sintering. This project leverages the unique UHS method to rapidly sinter dense layers of oxide ceramics from precursors in ~10 seconds by simply sandwiching ceramic pellets between two Joule-heated carbon films. This simple yet effective proximity heating strategy, with a temperature up to 2000-3000K enables a 10^2–10^4-fold acceleration in ceramic synthesis and sintering time; and provides a route for rapid verification and feedback to first-principles computational predictions, enabling a truly computation-guided, closed-loop materials discovery process. The UHS method is the fundamental technology behind the entrepreneurial start-up HighT-Tech, LLC, founded to make UHS a commercially relevant technology.

Publications and References

1. Fu, J., S. Wang, D. Wu, J. Luo, C. Wang, J. Liang, X. Lin, Y. Hu, S. Zhang, F. Zhao, W. Li, M. Li, H. Duan, Y. Zhao, M. Gu, T.K. Sham, Y. Mo, and X. Sun, Halide Heterogeneous Structure Boosting Ionic Diffusion and High-Voltage Stability of Sodium Superionic Conductors. Advanced Materials, 2024. 36(3). DOI: 10.1002/adma.202308012
2. Kwak, H., S. Wang, J. Park, Y. Liu, K.T. Kim, Y. Choi, Y. Mo, and Y.S. Jung, Emerging Halide Superionic Conductors for All-Solid-State Batteries: Design, Synthesis, and Practical Applications. ACS Energy Letters, 2022. 7(5): p. 1776-1805. DOI: 10.1021/acsenergylett.2c00438
3. Wang, S., J. Fu, Y. Liu, R.S. Saravanan, J. Luo, S. Deng, T.K. Sham, X. Sun, and Y. Mo, Design principles for sodium superionic conductors. Nature Communications, 2023. 14(1). DOI: 10.1038/s41467-023-43436-3

De Novo Proteins as Junctions in Polymer Networks

Lead Investigator: Alshakim Nelson, alshakim@uw.edu (coPI: David Baker, Lucas Meza, Monica Olvera-de la Cruz)
Participating Institutions: University of Washington, Northwestern University
Source of Support: Enter NSF-DMREF, DOE-BES, DOE-EERE, NIST, AFRL, AFOSR, or other support source.
Website: None
Keywords: Polymer network, de novo protein, mechanochemistry, stimuli-responsive materials, additive manufacturing

Project Scope

The central objective of this proposal is to elucidate the design principles for *de novo* designed proteins as mechano-responsive junctions in protein-polymer networks. The convergence of computational *de novo* protein design and materials science presents a unique opportunity to create protein-based thermosets that are superior to conventional synthetic materials. The structure and composition of designed proteins can be optimized to control the processability of the proteins (via additive manufacturing) and the bulk mechanical properties of the materials. This DMREF team will design and synthesize photocurable resins that form protein-polymer networks with de novo designed proteins as junctions, investigate *de novo* designed proteins as mechano-responsive junctions in polymer networks that unfold in response to a mechanical force, and create smarter/intelligent protein-polymer networks for the next generation of sustainable biomaterials.

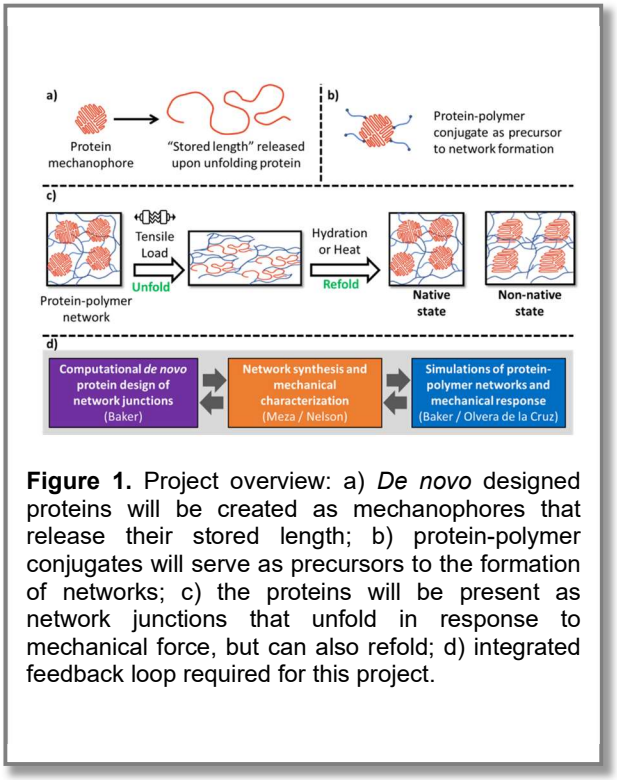


Figure 1. Project overview: a) *De novo* designed proteins will be created as mechanophores that release their stored length; b) protein-polymer conjugates will serve as precursors to the formation of networks; c) the proteins will be present as network junctions that unfold in response to mechanical force, but can also refold; d) integrated feedback loop required for this project.

Relevance to MGI

This project is developing new fundamental understandings of biohybrid materials by integrating protein design and engineering, polymer chemistry, and computational simulations. Thermosets are an important class of polymer network materials comprising polymer strands bound at their termini by covalent or noncovalent junctions. Proteins can serve as mechano-responsive junctions within thermosets, and these proteins can respond to extrinsic mechanical forces to release their stored length. The factors that determine the stored length include the nominal length of the outstretched protein, the number of strands per protein junction (junction valency), and the force required to mechanically unfold the protein. The topology of the protein-polymer network also serves an important role in the mechanical response of these materials. While the mechanical properties of these materials can be experimentally determined, computational simulations can provide critical insights into proteins unfolding and refolding in a network and ultimately accelerate the discovery of proteins for advanced materials.

Technical Progress

During Year 1 of this project, we have synthesized protein-polymer networks, characterized their mechanical properties, and used computational simulations to understand the response of these networks in response to mechanical loads. Our team has also established protocols for collaboration and material/knowledge transfer.

We designed and produced a series of stable twistless helix repeat (THR) proteins for establishing the initial design rules for developing protein-polymer networks. Our approach is modular and allows for additional helix repeat units to be incorporated. For example, most of our studies have utilized a THR with 3 repeat units, but we have also designed and expressed 5 helix-repeat constructs as well. In order to begin to understand how proteins can be designed as junctions in a polymer network, we first controlled the number of lysines present on the protein

for functionalization. Our first design included lysines only at the C and N termini. The reason for selecting terminal functionalization is because extension of these chains will lead to the maximum release of stored length. These proteins were produced on the scale of 95 mg/mL (approximately 1 mL for each protein provided to the team).

We are also investigating two approaches to synthesizing protein-polymer networks. In the first, we are using proteins conjugated with acrylate groups that are polymerized via a chain-growth mechanism. In the second, we are using thiol-containing proteins and telechelic PEG chains with terminal alkenes to fabricate networks via a step-growth mechanism. During this award period we have focused on the chain-growth approach. We have successfully incorporated the THR with 3 repeat units into a PEG-diacrylate network. We have cast dogbones and performed tensile measurements on these samples and observed that the modulus and failure strain increased with increasing amounts of protein. Resin optimization for 3D printing on a Nanoscribe two-photon printer is ongoing.

Simulations of the protein-polymer networks comprising the THR proteins are underway. Our initial simulations show that when the sample undergoes mechanical extension, mechanical failure occurs with the PEG portions of the network before the proteins can be mechanically unfolded. These results suggest that a larger fraction of protein is required in the network, a stiffer network structure is required in the network, and/or the energy required to unfold the protein is too high.

Future Plans

We will design and express THR proteins with additional functional group sites for attaching additional strands to the protein junctions. The additional attachment points may lead to more effective distribution of stress toward these proteins. Additional structural characterization by FTIR and SAXS is also in progress.

Broader Impacts and Workforce Development

The work proposed herein is, of necessity, interdisciplinary in nature and transcends protein engineering, biophysics, computer science, polymer science, mechanical engineering, and chemical engineering. The proximity of the Baker, Meza, and Nelson labs facilitates cross-pollination and training of DMREF trainees at the UW. The team has monthly Zoom meetings for providing scientific updates from each team member. This cross-disciplinary training will develop the next generation workforce with the scientific and digital literacy required for tackling future challenges.

Data Management and Open Access

A complete description of all synthetic procedures and characterization methods will be published along with the associated data. All data related to the characterization or processing of the polymers and proteins will also use the same labeling scheme, such that the source of the polymer or protein is always known. The interdisciplinary nature of our project will also produce a diversity of raw data, Foldit and Rosetta algorithms, functional gene and protein sequence information, on-line training videos, and presentations of a tremendous variety. We expect to produce massive computational protein design data, not all of which can or should be stored permanently. All directories and files will be kept on network drives that are backed up daily. Internal databases describing both validated and unvalidated designed proteins, design algorithms, and atomic coordinate files for protein designs will be maintained at the Institute for Protein Design.

Advancing Along the Materials Development Continuum and Partnerships to Translation

This project will accelerate the discovery and deployment of proteins as junctions in polymer networks for biohybrid plastics and engineering bioplastics. This project will also accelerate the identification and production of *de novo* proteins for advanced manufacturing processes such as additive manufacturing; additive manufacturing will accelerate application of these materials via rapid prototyping. The fundamental contributions of this project include a *de novo* protein design library that will enable the computational design of proteins that elicit a predetermined mechanical response. And finally, we will address the scaling issue of *de novo* proteins by designing polymer networks that can utilize as little as 5 w/w% proteins as network junctions. This project will also develop methods to evaluate the mechanical properties of protein-polymer networks on the microgram to milligram scale. Thus, a larger array of *de novo* designed proteins can be evaluated before a subset is selected for larger scale production.

Publications and References

N/A

Materials Architected by Adaptive Processing

Lead Investigator: Thao (Vicky) Nguyen[1], vicky.nguyen@jhu.edu, Gretar Tryggvason[1], David Elbert[1], Peter Olmsted[2], David Kazmer[3], Kalman Migler[4], Jonathan Seppala[4], Hilmar Koerner[5]
Participating Institutions: Johns Hopkins University[1], Georgetown[2], University of Massachusetts Lowell[3], NIST[4], AFRL[5]
Keywords: polymer processing, recycled polymer, immiscible blends, flow-induced crystallization.

Project Scope
The manufacturing of polymer materials from recycled feedstock is severely constrained by compositional uncertainties in the feedstock material, which can drastically alter the properties of the processed materials. The project seeks a data-centric approach for integrated materials design and manufacturing for application to polymer blends of recycled polyethylene (PE) and polypropylene (PP). We first characterize real recycled polyolefin blends, then investigate the ability to manipulate the melt streams through layer-multiplying elements and novel shape-multiplying elements to improve and assure the material properties.

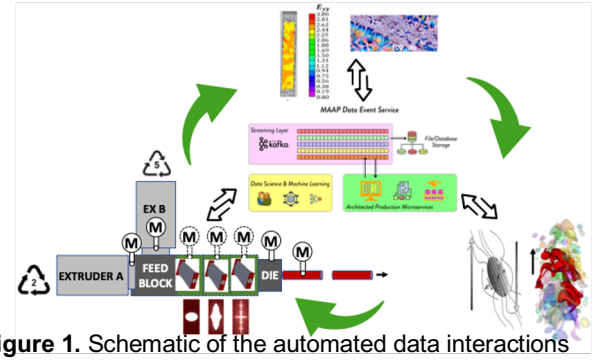


Figure 1. Schematic of the automated data interactions of the processing, characterization, and modeling tasks through an event-driven microservices data layer.

Relevance to MGI
An instrumented multi-layer extrusion process with modular shape-multiplying elements is designed with modeling studies to investigate the controllability of the architected blends. Multiscale modeling is being used to study the flow-induced crystallization of the multi-component melt, the stability of the melt streams, and the formation of phase domains during processing to determine how the measurable processing parameters control the crystalline morphologies and domain architecture. To tie these activities together, we are creating event-driven, microservices data layer to automate the contextualized data flow between the different processing, characterization, and modeling tasks of the project. This approach maximizes productivity and collaboration with machine learning advances while reducing uncertainty from design to production. The same data and data infrastructure applied for materials design is harnessed for process monitoring and control to ensure consistent production of materials with targeted properties.

Technical Progress
Our studies have thus far focused on 3 interrelated tasks: 1) developing an events-driven data service to automate the contextualized data flow from the various process, characterization, and modeling tasks; 2) characterizing the effect of compositional variability of a recycled polyethylene feedstock on the thermomechanical properties of manufactured polymer film; and 3) modeling the flow behavior of the multicomponent melt.

The data team, led by Elbert, has expanded the OpenMSI Stream architecture to perform extract-transform-load (ETL) polymer film processing data from UMass, Lowell (UML). Data from the film extruder is now streaming live to the data infrastructure at JHU and consumed as both archived CSV files and loaded into a SQL database available through REST API in the SciServer data system. The data includes over 91,374 rows of temperature, pressure, and flow rate from different locations of the melt stream, as well as from a video camera to estimate the thickness and properties of the cooled film in real time during processing. We have updated the schema and created a bespoke data consumer (https://github.com/openmsi/dmrefplastics) to respond to format changes from the process controller. The team has also contributed to the first release of the OpenMSIModel Python package (https://github.com/openmsi/openmsimodel) to create an automated instantiation of the graphical data model developed in year one. The graph model provides a unifying semantic description between the processing, characterization, and modeling portions of the project. The data team is also working with our NIST collaborators to develop machine learning methods to accelerate data reduction and understanding of crystallization processes.

A primary challenge of working with recycled polymer feedstock is the inherent variability and uncertainty in the recycled feedstock, which must be characterized and controlled during processing to ensure consistent

production. The processing and characterization teams, led by Kazmer and Nguyen, are investigating methods for characterizing the rheological and thermomechanical properties of recycled polyolefin feedstock and the effect of compositional variability on the mechanical properties of the extruded films. We are working with two recycled polypropylene supplies containing unknown quantities of polyethylene. Through a series of experiments, we determined that DSC provides a straightforward and reproducible method for identifying the relative weight fraction and type of PE (e.g., HDPE, LDPE, etc.) in the PP recyclate. The Kazmer team also identified FTIR as a promising high-fidelity approach for online identifying compositional variations in the PP recyclate. Kazmer also showed that melt flow rate (MFR) of a material/blend was a poor predictor of its processing behavior. Large variations were observed in the processing of different polyolefins blends with relatively similar MFR and viscosity behaviors. Characterization experiments by the Nguyen team showed that the weight fraction of PE significantly affected the degree of crystallinity and the strength and ductility of the films in the perpendicular direction to the flow. We are performing DSC and wide-angle x-ray scattering studies with NIST and AFRL collaborators to investigate the role of the degree of crystallinity and dispersion of the PE domains (from polarized light microscopy) on the properties.

The Tryggvason team's modeling effort is ongoing to investigate the effect of blend rheology on the melt flow. We have conducted several simulations examining the mixing of two polymer melts at low Reynolds numbers for a variety of volume fraction ratios and Weissenberg numbers. Current results for pressure driven parallel flows containing a dispersion of drops of one polymer in another show that while the mixing is relatively uniform across most of the channel, the continuous polymer forms a pure film at the walls. We are currently examining the effect of the drop size and the Weissenberg number, as well implementing material models for the cooling.

Future Plans

In the coming year, the processing and characterization tasks will begin to evaluate the ability of the layer multiplying elements to redistribute and homogenize the components of the melt blend and alter the degree of crystallinity of the PE and PP components. Computational modeling of the multicomponent melt will incorporate cooling and crystallization. The data team will continue to develop ML methods to analyze data from NIST and discover the crystallization kinetics of multicomponent melts. Following model development and training, the learner will be deployed at NIST on the streaming backbone to provide data extraction in real-time.

Broader Impacts and Workforce Development

This project has supported for 4 graduate students and 2 postdoctoral fellows, all are either women or from groups underrepresented in engineering. Alex Watson Jones successfully submitted her Master's thesis, and both Becca Olanrewaju and Sixtus Nzeh passed their PhD candidacy exams. The data and methods of this project has also supported outreach efforts at JHU and UML through the WISE program and the plastics sustainability forum.

Data Management and Open Access

Our project plan includes use of a single, unified semantic description of data. This allows use of a single database of metadata to describe and provide access to the entire project. Structured data will be hosted in SQL databases, while unstructured data (e.g., image files) will be curated in cloud-based storage. During the lifetime of the project, data will be maintained and hosted at Johns Hopkins University (JHU) by the Institute for Data Intensive Engineering and Science (IDIES). In MAAP-DESc, files are processed by an asynchronous data broker triggering metadata harvesting, the population of our sample description database, creation of DOIs, and movement of files to SciServer's petabyte-capable cloud storage. The automatic population of our metadata database makes data immediately findable, accessible, and reusable to the project.

Advancing Along the Materials Development Continuum and Partnerships to Translation

A core strength of the project is the integration between designing the material and process control for the constituent production of the material. This will facilitate the translation to support commercial recycling.

Publications and References

- D.O. Kazmer, S.O. Nzeh, B. Shen, D.C. Elbert, T.D. Nguyen, "Characterization, processing, and modeling of industrial recycled polyolefins", submitted to Polymer Engineering and Science in March 2024.
- Watson Jones, "Characterization and Microstructural Analysis of Recycled Polypropylene Films", Thesis for the degree of Master of Science in Engineering, Johns Hopkins University, December 2023.

Developing High-Performance TDDFT Codes, Theories and Validation Efforts for Ultrafast Phenomena in Materials

Lead Investigator: Tadashi Ogitsu, ogitsu1@llnl.gov
Participating Institutions: Lawrence Livermore National Lab, Stanford/SLAC, University of Wisconsin Madison, Lawrence Berkeley National Lab.
Source of Support: DOE-BES.
Keywords: DFT, TDDFT, Ultrafast, Magnetism.

Project Scope

NPNEQ develops several open-source softwares designed for the simulation of materials under different conditions. Among these, INQ is specifically designed to solve the Density Functional Theory (DFT) and Time Dependent Density Functional Theory problems on graphic processing units (GPU). Besides the GPU support INQ makes use of modern code design features and results in a concise but complete DFT/TDDFT implementation of roughly 12000 lines of C++ code.

These new developments open the way for a fully ab-initio description of the dynamics of electrons and spins and their coupling to the atomic degrees of freedom. This is relevant to a wide range of applications, including the design of switching, memory and optoelectronic devices, in addition to new materials processing methods.

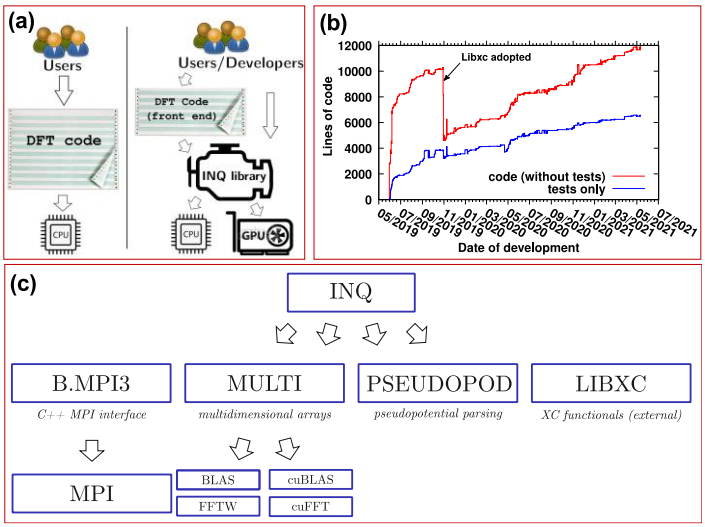
Relevance to MGI

Recent advances in high performance computing (HPC) have provided a new platform to model materials at the atomic scale using DFT and ab-initio Quantum Molecular Dynamics (QMD).
The possibility to simulate the evolution of materials in real time under different conditions can be used to guide experiment design. This idea of extreme interconnection between experiments and theory has lead to the development of the multi-disciplinary Center for Non-Perturbative Studies of Functional Materials under Non-Equilibrium Conditions (NPNEQ).
The center focuses on the development of scalable software to help interpret complex experimental data and it supports the development of ab-initio studies of materials far from equilibrium driving advances in areas like non-equilibrium dynamics of quantum materials, strong field attosecond physics and warm dense matter.
The case of warm dense matter is particularly striking. This is an extreme state of matter at the confluence between the solid state and the plasma state. The electrons in the warm dense regime are not free particles and cannot be treated as a gas of classical particles. Correlation effects are still important in this regime and on the theory side we need to account for quantum effects.

At the same time, on the experimental side, the difficulty to create such extreme state of matter in the laboratory requires the experiment to be constantly informed by theory. Our unique capabilities to describe such extreme states of matter will have a huge impact in the field and provides information useful to the design of new experiments.

Technical Progress

We can list the following recent developments: (1) The implementation of real time dynamics using hybrid functionals; (2) the inclusion of spin non collinear effects with important implications for spin dynamics and the study of out of equilibrium spin dynamics; (3) Support for Nvidia GPU (Lassen at LLNL and Perlmutter at NERSC) and AMD MI250 GPU (Frontier at Oak Ridge) MI300 APU (El Capitan at LLNL); (4) Interactive user interface including ASE (Python).



Future Plans

We are working on a more complete description of spin dynamics. This requires the implementation of spin orbit coupling and other non collinear effects like more accurate exchange-correlation fields. We will focus on the implementation of magnon spectra and on the effects of decoherence coming from the coupling between spins and phonons[2,3,4] in addition to the direct coupling between spins and light.

Broader Impacts and Workforce Development

One of the main purpose of the INQ code development is to make the use of DFT and TDDFT for material simulations easily accessible to a wide range of researchers within the community. The code is designed around algorithms and numerical libraries rather than around specific implementations, making its use simpler and a perfect interface for higher level post-processing tools.

Data Management and Open Access

The INQ code can be directly accessed from: NPNEQ / inq · GitLab

Advancing Along the Materials Development Continuum and Partnerships to Translation

The numerical methods we are developing allow to simulate material properties with much higher level of accuracy compared to non ab-initio methods. Many of these properties are difficult to obtain directly from experiments, in addition, the complexity of such experiments often requires additional interpretation of the results. The combination of such accumulated numerical and experimental data will produce a wealth of information from which target-specific experiments and simulations can be further planned.

Publications and References

- [1] Xavier Andrade, Chaitanya Das Pemmaraju, Alexey Kartsev, Jun Xiao, Aaron Lindenberg, Sangeeta Rajpurohit, Liang Z. Tan, Tadashi Ogitsu and Alfredo Correa, *Inq, a Modern GPU-Accelerated Computational Framework for (Time-Dependent) Density Functional Theory*, Journal of Chemical Theory and Computation **17**, 7447 (2021). DOI: 10.1021/acs.jctc.1c00562 .
- [2] Junqing Xu and Yuan Ping, *Ab Initio Predictions of Spin Relaxation, Dephasing and Diffusion in Solids*, Journal of Chemical Theory and Computation 20, 492 (2024). DOI: https://doi.org/10.1021/acs.jctc.3c00598
- [3] Junqing Xu, Kejun Li, Uyen N. Huynh, Mayada Fadel, Jinsong Huang, Ravishankar Sundararaman, Valy Vardeny and Yuan Ping, How spin relaxes and dephases in bulk halide perovskites, Nature Communications 15, 188 (2024).
- [4] M. Mo, A. Tamm, E. Metsanurk, Z. Chen, L. Wang, M. Frost, N. Hartley, F. Ji, S. Pandolfi, A. Reid, P. Sun, X. Shen, Y. Wang, X. Wang, S. Glenzer, A. A. Correa, *Direct observation of strong momentum-dependent electron-phonon coupling in a metal*, Science Advances **10**, eadk9051, (2024) DOI:10.1126/sciadv.adk9051.
- [5] W. Hayami, T. Hiroto, K. Soga, T. Ogitsu, K. Kimura, *Thermodynamic stability of elemental boron allotropes with varying numbers of interstitial atoms*, Journal of Solid State Chemistry **329**, 124407 (2024) DOI:10.1016/j.jssc.2023.124407.
- [6] T. Hiroto, Y. Morino, M. Yoshikawa, K. Soga, W. Hayami, T. Ogitsu, K. Kimura, *Does phonon induced structural change by beta-rhombohedral boron occur at room temperature?*, Solid State Sciences 142, 107246 (2023) DOI:10.1016/solidstatesciences.2023.107246.
- [7] S. Rajpurohit, T. Ogitsu, L. Tan, *Ballistic photocurrent driven by optical phonon modes in a polaronic ferroelectric*, Phys. Rev. B 108, 104305 (2023).
- [8] S. Rajpurohit, C. Joose, S. Techert, T. Ogitsu, P.E. Blochl, L.Z. Tan, *Characteristic THz-emissions induced by optically excited collective orbital modes*, arXiv preprint arXiv:2306.09107.
- [9] V. Pareek, D. R. Bacon, X. Zhu, Y.-H. Chan, F. Bussolotti, N. S. Chan, J. P. Urquizo, K. Watanabe, T. Taniguchi, M. K. L. Man, J. Madéo, D. Y. Qiu, K. Eng J. Goh, F. H. da Jornada, K. M. Dani, *Driving non-trivial quantum phases in conventional semiconductors with intense excitonic fields*, arXiv preprint arXiv:2403.08725 (under review).
- [10] G. de la Peña Muñoz, A.A. Correa, S. Yang, O. Delaire, Y. Haung, A.S. Johnson, T. Katayama, V. Krapivin, E. Pastor, D.A. Reis, S. Taitelbaum, L. Vidas, S. Wall, M. Trigo, *Ultrafast lattice disordering can be accelerated by electronic collisional forces*, Nature Physics **19**, 1489-1494 (2023). DOI:10.1038/s41567-023-02118-z.

DMREF: Accelerating the Adoption of Sintering-Assisted Additive Manufacturing Using Integrated Experiments, Theory, Simulation and Data Science

Lead Investigator: Eugene A. Olevsky, eolevsky@sdsu.edu, Rajendra K. Bordia, rbordia@clemson.edu, Lisa Rueschhoff,lisa.rueschhoff.1@us.af.mil
Participating Institutions: San Diego State University, Clemson University, AFRL
Website: https://dmref.sdsu.edu/
Keywords: Additive manufacturing, sintering, multi-scale simulations, machine learning.

Project Scope

The overarching goal of the proposed research is the development of a new type of experimentally guided and validated multi-scale direct and inverse sintering model taking into account specifics of micro- and macro structure in the SAAM processes (Fig. 1). The solution to this fundamental inverse sintering problem enabling the determination of the optimal green state processing conditions; pre-sintering components' shape, and micro- and macro-structure; and sintering conditions required to obtain the desired shape and microstructure, - is the ultimate objective of this project.

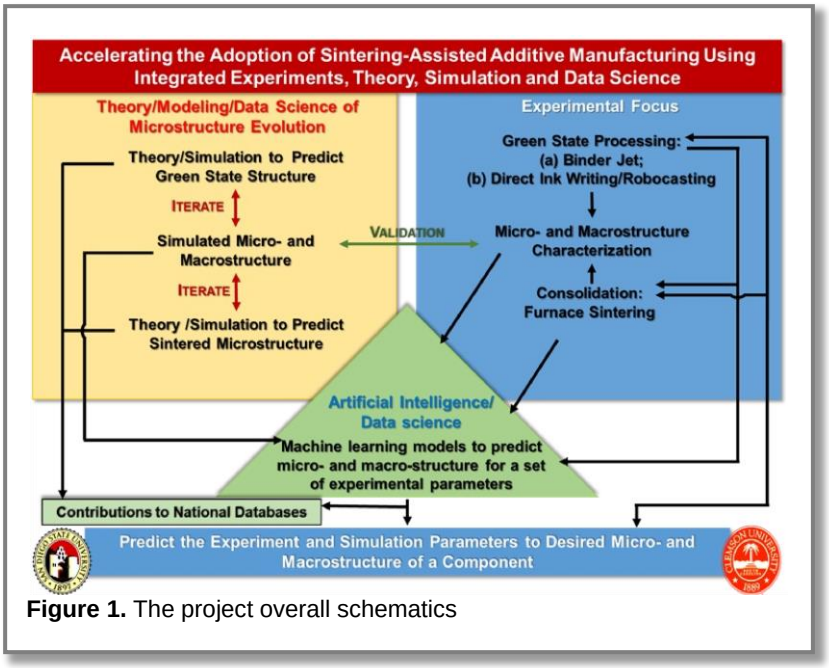


Figure 1. The project overall schematics

Relevance to MGI

The proposed integration of computation and experiments in a data-driven predictive framework addresses the complex interplay between green-state processing conditions and anisotropic microstructure. The conducted research projects aimed to provide fundamental, basic knowledge and a novel practical approach to design and optimize the manufacturing of advanced ceramic systems with programmable macroscopic characteristics and microstructure and hence properties and performance.

Technical Progress

The effects of powder bed creation and powder spreading in binder jetting technology have been studied through experiments and models. An experimentally validated discrete element method (DEM) model was developed to observe how powder spreading parameters influence the formation of distortions in printed parts [1]. Additionally, a DEM model for powder deposition and spreading has been used to study how the process and particle size distribution affect the generation of non-uniformities, such as density variation and particle segregation [2].

The micro- [3-6] and macrostructure [7-8] evolution of 3D-printed metallic materials have been investigated experimentally. Models for different process steps have been developed to provide both real and "virtual" experimental data for machine learning algorithms.

High-resolution synchrotron X-ray computed tomography (SXCT) analysis of binder jetting (BJT) 316L samples from ex-situ interrupted sintering tests highlighted, for the first time, the presence of periodic density fluctuations along the building direction. These density fluctuations in the porous body and the microstructural evolution during sintering can be linked to the anisotropic shrinkage typical of components manufactured through binder jetting technology [3,4].

The macrostructure evolution during sintering, besides being influenced by anisotropic shrinkage, is also affected by external factors such as gravity and friction [7-10]. The influence of these factors has been investigated both experimentally and analytically through the creation of a sintering model, which includes these influences and has

shown the potentiality to be used in the development of strategies to compensate for distortion in sintered components [10,11].

Different Machine Learning algorithms were compared for image-based porosity classification from a diverse and complex porosity image set. Within them Deep Convolutional Neural Network (DCNN) performed with the highest accuracy, shown simplicity of the model, and a variety of materials and defects can be easily included in the model by simply adding a new training dataset [12].

An image based automated porosity detection methods on a limited dataset has been developed. A generative adversarial neural network (GAN) has been used to augment the dataset and then two CNNs - Faster R-CNN and YOLOv5 – have been trained [13]. A grain boundary detection for sintered 3D-printed metal parts based on UNets machine learning method has been developed. The developed methods showed an accuracy around 90% for unclear GB images and 92% for clear GB images [14].

To augment the experimental data of green component microstructures, we employed generative learning techniques for construction of digital twins. We found that training of a Wasserstein GAN with gradient penalty can be further stabilized by using an adaptive discriminator. We have investigated the capabilities of WGAN-GP when applied to images of anisotropic porous ceramics. We have leveraged images of hierarchical anisotropic porous electrodes manufactured in PI Bordia's lab at Clemson.

For research on robocasting of ceramics, a new machine designed by our partner, Robocasting Enterprises., has been installed and is operational at Clemson University. We have been investigating the isotropic densification behavior of slip cast ceramics as a baseline against which the robocast samples will be compared.

Future Plans

- The development of a new constitutive model of sintering of AM ceramics based on the mutual calibration of the meso-scale sintering simulation code, experiments, and the machine learning of the specifics of the green and sintered microstructure of the SAAM produced parts.
- Development of constrained generative AI models that allow selective generation of virtual microstructures for specific processing conditions which will ultimately enable prediction of microstructures for unknown/unexplored processing parameters.
- The solution of the "inverse" problems of sintering enabling the determination of the optimal AM conditions, and green components' shape and micro- and macro-structure required to obtain the desired shape and micro-structure of the sintered component.
- Validation implementation of developed simulation platforms for SAAM produced components of interest to AFRL and industrial partners.

Broader Impacts and Workforce Development

Since the beginning of the project, at SDSU 7 Ph.D. students were involved in the project, including one African, one Hispanic female, one Iranian female, one Asian, one Spanish and one American. Moreover, two postdoctoral fellows from Europe, France and Ukraine, were involved. At Clemson University, one Asian female PhD student and two male Asian postdoctoral scholars have contributed to this project. One Asian female graduate student in Schiller's group was supported by this award in 2022-2023. One Asian male PhD student was hired in January 2024 at University of Delaware to continue the work on the implementation and deployment of generative machine learning approaches.

Data Management and Open Access

The primary analyzed data will be published in the form of peer-reviewed journal articles, theses, and other print or electronic publishing formats (e.g., pdf format). In addition, the associated metadata that describes the theoretical models and data analysis methods, experimental setups, fabrication procedures, will be made available in materials databases and repositories for re-use by the scientific community. Accompanying workflow descriptions will be released as educational materials through the NSF sponsored Nanohub platform. Co-PI Schiller, in collaboration with The Carpentries, has developed and taught the Data Carpentry Curriculum on Image Processing with Python, which is openly available on the Data Carpentry website [15-16]. To aid citation of software and data, the PIs will secure digital object identifiers (DOI) where possible.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Our team has close interaction with two industrial partners (California Nanotechnologies and Robocasting Enterprises). Both partners have shown significant interest in translating the research in this fundamental project to their programs. In order to conduct this focused developmental work, we have submitted two GOALI supplemental funding requests.

Publications and References

1. O.P. Maidaniuk, A.L. Maximenko, D. Olumor, E. Torresani, M.B. Shtern, E. Olevsky, *Modeling of Powder Bed Deformation in the Binder Jetting Technology*. Powder Metallurgy and Metal Ceramics, **61(1)**, 1-8, (2022)
2. T. Grippi, A. Maximenko, A. Cabo Rios, E. Torresani, E. Olevsky, *Non-uniformity of spread layers in binder jetting additive manufacturing*, (in preparation)
3. A. Cabo Rios, E. Hryha, E. Olevsky, P. Harlin, *Sintering anisotropy of binder jetted 316L stainless steel: part I–sintering anisotropy*, Powder Metallurgy, **65(4)**, 273-282 (2022)
4. A. Cabo Rios, E. Hryha, E. Olevsky, P. Harlin, *Sintering anisotropy of binder jetted 316L stainless steel: part II–microstructure evolution during sintering*, Powder Metallurgy, **65(4)**, 283-295, (2022)
5. A. Cabo Rios, E. Olevsky, E. Hryha, M. Persson, R.K. Bordia, *Analytical models for initial and intermediate stages of sintering of additively manufactured stainless steel*. Acta Materialia, **249**, 118822, (2023)
6. A. Cabo Rios, T. Mishurova, L. Cordova, M. Presson, G. Bruno, E. Olevsky, E. Hryha, *Ex-situ characterization and simulation of density fluctuations evolution during sintering of binder jetted 316L*. Materials & Design, **238**, 112690 (2024)
7. E. Torresani, R.M. German, R. Huff, E.A. Olevsky*, Influence of gravity on sintering of 3D-printed powder components.* Journal of the American Ceramic Society, **105(1)**, 131-146 (2022)
8. A. Cabo Rios, M. Persson, E. Hryha, E. Olevsky, *Phenomenological sintering model and experimental validation of gravity-induced distortions in binder-jetted stainless-steel components*. Ceram. Int. (2024). DOI: https://doi.org/10.1016/j.ceramint.2024.04.427
9. T. Grippi, E. Torresani, A. Cabo Rios, A. L. Maximenko, M. Zago, I. Cristofolini, A. Molinari, R.K. Bordia, E.A. Olevsky, *Mitigation of gravity-induced distortions of binder-jetting components during rotational sintering*. Additive Manufacturing Letters, **10**, 100215, (2024)
10. E. Torresani, A. Cabo Rios, T. Grippi, A.L. Maximenko, M. Zago, I. Cristofolini, E.A. Olevsky, *Sintering Model for Predicting Distortion of Additively Manufactured Complex Parts*, Rapid Prototyping Journal (submitted)
11. M. Zago, T. Grippi, A. Cabo Rios, E. Torresani, A.L. Maximenko, I. Cristofolini, E.A. Olevsky, *Sintering Compensation Strategies of 316L Pipe Tee Connectors Printed by Binder Jetting Additive Manufacturing* (in preparation)
12. N. Satterlee, E. Torresani, E. Olevsky, J. Kang, *Comparison of machine learning methods for automatic classification of porosities in powder-based additive manufactured metal parts*, Int J Adv Manuf Technol, **120**, 6761–6776 (2022).
13. N. Satterlee, E. Torresani, E. Olevsky, J. Kang, *Automatic detection and characterization of porosities in cross-section images of metal parts produced by binder jetting using machine learning and image augmentation.* Journal of Intelligent Manufacturing**, 35(3)**, 1281-1303, (2024)
14. N. Satterlee, R. Jiang, E. Olevsky, E. Torresani, X. Zuo, J.S. Kang, *Robust image-based cross-sectional grain boundary detection and characterization using machine learning.* J Intell Manuf, 1-29, (2024) DOI: https://doi.org/10.1007/s10845-024-02383-6
15. Schiller, U., *Image Processing with Python.* Zenodo (2024) DOI: https://doi.org/10.5281/zenodo.10547352
16. The Carpentries; M. Meysenburg, T.D. Brooks; R. Burks.; D. Palmquist; U. Schiller, *Data Carpentry Image Processing Data.* figshare. Dataset (2023). DOI: https://doi.org/10.6084/m9.figshare.19260677.v3

MatSciLLM leaderboard: An evaluation of Large Language Models in Material Science

Vineeth Venugopal, Aleyna Beste Ozhan, Elsa Olivetti

Massachusetts Institute of Technology

Lead Investigator: Elsa Olivetti, elsao@mit.edu

Participating Institutions: Massachusetts Institute of Technology

Source of Support: NSF-DMREF

Website: NONE

Keywords: Large Language Models, NLP, Data, Artificial Intelligence, Knowledge Graph

Project Scope

The DMREF project aims to accelerate materials discovery and synthesis through the integration of data-driven methods and experimental validation. We have developed a precursor recommendation engine and machine-learning models to predict synthesis conditions, focusing on solid-state synthesis and zeolitic materials. Our project leverages a comprehensive synthesis database, created through advanced text-mining techniques, to provide accurate and efficient recommendations for novel material synthesis. We have validated these recommendations experimentally, achieving high success rates in synthesizing target materials. Additionally, our zeolite synthesis work includes the creation of an Organic SDA Database for high-throughput binding energy calculations, facilitating the selection of optimal structure-directing agents. This project not only advances the understanding and application of synthesis science but also contributes to the broader research community by providing open access to our data, algorithms, and tools. Our ultimate goal is to streamline the synthesis process, reduce costs, and enhance the efficiency of materials development, thereby significantly advancing the field of materials science.

Relevance to MGI

The DMREF project aligns with the 2021 MGI strategic plan by integrating experiment, computation, and theory in a closed, iterative feedback loop. We combine machine-learning models, data extraction methods, and experimental validation to enhance synthesis science. The synthesis recommendation engine, developed through collaboration between MIT, UC Berkeley, and UMass Amherst, exemplifies this integration. Our project involves continuous interaction among synthesis, characterization, and computational modeling. Data-driven insights from literature mining inform experimental designs, while experimental outcomes refine our algorithms, ensuring accurate predictions. The zeolite synthesis case study showcases this iterative process, where data analytics, simulation, and experimental validation work synergistically. Our Organic SDA Database and high-throughput synthesis platform exemplify how computational predictions guide experimental efforts, leading to efficient synthesis of desired materials. This approach has significantly advanced our understanding of precursor selection and synthesis

conditions. By building a robust synthesis database and developing predictive models, we accelerate materials discovery and development. The project's outputs—open-access datasets, algorithms, and tools—foster a collaborative research environment, enabling the design of materials with specific functions or properties. This iterative, integrative approach ensures continuous improvement and contributes to a fundamental knowledge base, driving innovation in materials science.

Technical Progress

In the past year, the MatSciLLM Leaderboard project has made significant strides in benchmarking the performance of Large Language Models (LLMs) in Materials Science. We have developed a robust evaluation framework that systematically assesses the capabilities of various LLMs on critical tasks such as property prediction, ontology understanding, and semantic analsysis. This framework ensures consistent and fair comparisons between different models, thereby providing a clear understanding of their strengths and limitations. We develop several novel datasets collected from several sources including over 5 Million materials science papers using advanced text-mining techniques. This dataset serves as the foundation for our benchmarking efforts, offering a comprehensive and diverse set of examples for model evaluation.

Future Plans

The MatSciLLM Leaderboard project aims to expand its scope and impact by enhancing the benchmarking framework and increasing community engagement. In the coming year, we plan to extend our evaluation framework to cover a broader range of materials science tasks, including advanced property prediction and process optimization. This will involve the integration of more diverse datasets and the inclusion of newer LLMs as they become available. A significant focus will be on developing a community-driven platform where researchers can contribute data, models, and insights, fostering collaboration and continuous improvement.

Broader Impacts and Workforce Development

The MatSciLLM Leaderboard project aligns with the MGI Strategic Plan's goal of educating, training, and connecting the materials R&D workforce. To educate and train the next generation of scientists, we have developed comprehensive tutorials and training materials that cover the use of LLMs in materials science. These resources are designed to help researchers, students, and industry professionals understand and apply advanced AI techniques to their work. By hosting regular workshops and webinars, we provide hands-on training and foster a collaborative learning environment.

Data Management and Open Access

In alignment with the MGI Strategic Plan's objective to harness the power of materials data, the MatSciLLM Leaderboard project implements All project data, code, and results will be made openly accessible to the community through public repositories. Our datasets, benchmarking results, and predictive models will be available on platforms such as GitHub and the Materials Project, ensuring that researchers worldwide can access and utilize our resources.

Publications and References

1. Jensen, Zach, Edward Kim, Soonhyoung Kwon, Terry ZH Gani, Yuriy Román-Leshkov, Manuel Moliner, Avelino Corma, and Elsa Olivetti. "A machine learning approach to zeolite synthesis enabled by automatic literature data extraction." ACS central science 5, no. 5 (2019): 892-899.
2. Schwalbe-Koda, D., Kwon, S., Paris, C., Bello-Jurado, E., Jensen, Z., Olivetti, E., Willhammar, T., Corma, A., Román-Leshkov, Y., Moliner, M. and Gómez-Bombarelli, R., 2021. A priori control of zeolite phase competition and intergrowth with high-throughput simulations. Science, 374(6565), pp.308-315.
3. Jensen, Z., Kwon, S., Schwalbe-Koda, D., Paris, C., Gómez-Bombarelli, R., Román-Leshkov, Y., Corma, A., Moliner, M. and Olivetti, E.A., 2021. Discovering relationships between OSDAs and zeolites through data mining and generative neural networks. ACS Central Science, 7(5), pp.858-867.
4. "An instance level approach for shallow semantic parsing in scientific procedural text." Daivik Swarup, Ahsaas Bajaj, Sheshera Mysore, Tim O'Gorman, Rajarshi Das, and Andrew McCallum. In Findings of the Association for Computational Linguistics: EMNLP 2020, https://aclanthology.org/2020.findings-emnlp.270/
5. "MS-Mentions: Consistently Annotating Entity Mentions in Materials Science Procedural Text." Tim O'Gorman, Zach Jensen, Sheshera Mysore, Kevin Huang, Rubayyat Mahbub, Elsa Olivetti, and Andrew McCallum. Association for Computational Linguistics 2021, https://aclanthology.org/2021.emnlp-main.101/
6. "CSFCube - A Test Collection of Computer Science Research Articles for Faceted Query by Example", Sheshera Mysore, Tim O'Gorman, Andrew McCallum, Hamed Zamani. NeurIPS 2021 Datasets and Benchmarks Track (2021). https://arxiv.org/abs/2103.12906
7. "Multi-Vector Models with Textual Guidance for Fine-Grained Scientific Document Similarity", Sheshera Mysore, Arman Cohan, Tom Hope, North American Chapter of the Association for Computational Linguistics 2022 https://aclanthology.org/2022.naacl-main.331/
8. "Inducing and using alignments for transition-based AMR parsing." Andrew Drozdov, Jiawei Zhou, Radu Florian, Andrew McCallum, Tahira Naseem, Yoon Kim, and Ramon Fernandez Astudillo. North American Chapter of the Association for Computational Linguistics 2022, https://aclanthology.org/2022.naacl-main.80/
9. "Augmenting Scientific Creativity with Retrieval across Knowledge Domains", Hyeonsu B. Kang, Sheshera Mysore, Kevin Huang, Haw-Shiuan Chang, Thorben Prein, Andrew McCallum, Aniket Kittur, Elsa Olivetti, NLP+HCI Workshop at North American Chapter of the Association for Computational Linguistics 2022, https://arxiv.org/abs/2206.01328
10. "Unsupervised Partial Sentence Matching for Cited Text Identification", Kathryn Ricci, Haw-Shiuan Chang, Purujit Goyal, Andrew McCallum, Third Workshop on Scholarly Document Processing at Association for Computational Linguistics 2022, https://aclanthology.org/2022.sdp-1.11/
11. "Multi-CLS BERT: An Efficient Alternative to Traditional Ensembling", Haw-Shiuan Chang, Ruei-Yao Sun, Kathryn Ricci, Andrew McCallum, Under Submission at ACL 2023, https://arxiv.org/abs/2210.05043

12. "How Data Scientists Review the Scholarly Literature", Sheshera Mysore, Mahmood Jasim, Haoru Song, Sarah Akbar, Andre Kenneth Chase Randall, Narges Mahyar, ACM SIGIR Conference On Human Information Interaction And Retrieval 2023, https://arxiv.org/abs/2301.03774
13. Tanjin He, Wenhao Sun, Haoyan Huo, Olga Kononova, Ziqin Rong, Vahe Tshitoyan, Tiago Botari, and Gerbrand Ceder. "Similarity of precursors in solid-state synthesis as text-mined from scientific literature." Chemistry of Materials 32, no. 18 (2020): 7861-7873.
14. Elsa A. Olivetti, Jacqueline M. Cole, Edward Kim, Olga Kononova, Gerbrand Ceder, Thomas Yong-Jin Han, and Anna M. Hiszpanski. "Data-driven materials research enabled by natural language processing and information extraction." Applied Physics Reviews 7, no. 4 (2020): 041317.
15. Olga Kononova, Tanjin He, Haoyan Huo, Amalie Trewartha, Elsa A. Olivetti, and Gerbrand Ceder. "Opportunities and challenges of text mining in materials research." Iscience 24, no. 3 (2021): 102155.
16. Haoyan Huo, Christopher J. Bartel, Tanjin He, Amalie Trewartha, Alexander Dunn, Bin Ouyang, Anubhav Jain, and Gerbrand Ceder. "Machine-learning rationalization and prediction of solid-state synthesis conditions." Chemistry of Materials 34, no. 16 (2022): 7323-7336.
17. Zheren Wang, Olga Kononova, Kevin Cruse, Tanjin He, Haoyan Huo, Yuxing Fei, Yan Zeng et al. "Dataset of solution-based inorganic materials synthesis procedures extracted from the scientific literature." Scientific Data 9, no. 1 (2022): 231.
18. Zheren Wang, Kevin Cruse, Yuxing Fei, Ann Chia, Yan Zeng, Haoyan Huo, Tanjin He, Bowen Deng, Olga Kononova, and Gerbrand Ceder. "ULSA: Unified language of synthesis actions for the representation of inorganic synthesis protocols." Digital Discovery 1, no. 3 (2022): 313-324.
19. Tanjin He, Haoyan Huo, Christopher J. Bartel, Zheren Wang, Kevin Cruse, and Gerbrand Ceder. "Precursor recommendation for inorganic synthesis by machine learning materials similarity from scientific literature." Science Advances 9, no. 23 (2023): eadg8180.
20. Zheren Wang, Yingzhi Sun, Kevin Cruse, Yan Zeng, Yuxing Fei, Zexuan Liu, Junyi Shangguan, Young-Woon Byeon, KyuJung Jun, Tanjin He, Wenhao Sun, and Gerbrand Ceder. "Optimal thermodynamic conditions to minimize kinetic byproducts in aqueous materials synthesis." Nature Synthesis (2023) Accepted.
21. Sheshera Mysore, Mahmood Jasim, Andrew McCallum, and Hamed Zamani. "Editable User Profiles for Controllable Text Recommendation." in Proceedings of the 46th International ACM SIGIR Conference on Research and Development in Information Retrieval, 2023
22. Sheshera Mysore, Andrew McCallum, and Hamed Zamani. "Large Language Model Augmented Narrative Driven Recommendations." in Proceedings of the 17th ACM Conference on Recommender Systems, 2023

Accelerating Discovery of High Entropy Silicates for Extreme Environments

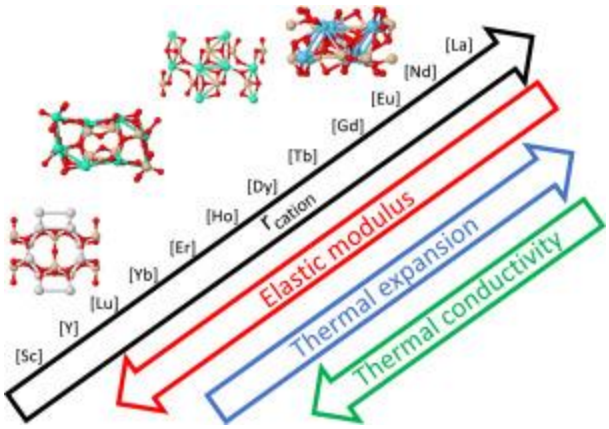
Lead Investigator: Elizabeth J. Opila, opila@virginia.edu
Participating Institutions: University of Virginia, University of Texas, Dallas, Rolls-Royce Corporation
Source of Support: NSF-DMREF
Website: none
Keywords: Rare earth silicates, high entropy, thermal conductivity, thermal expansion, thermochemical stability

Project Scope

A systematic exploration of fundamental stability, structure, and bonding of the individual rare earth silicates as well as multicomponent rare earth silicates was undertaken to accelerate materials discovery, and enable the opportunity to simultaneously tailor and optimize desired properties. We focus on determining melting temperature, thermal expansion, high temperature steam stability, stability with respect to molten siliceous debris, and thermal conductivity as a function of rare earth (RE) cation size for single and multiple RE cation silicates. We further investigate whether rule of mixtures can be used to predict properties for multicomponent RE silicates using both experimental and computational approaches.

Relevance to MGI

The computational methods utilized for predicting phase stability, bond strength, and resulting properties are at the core of our collaboration. Each property is calculated and explored experimentally with information provided back to the computational models. In addition, phase stability and properties are compared/contrasted between materials synthesized via solid state and sol-gel routes. Finally, correlations between properties as a function of rare earth cation size, average rare earth cation size, or standard deviation from rare earth cation size are correlated. For example, high modulus correlates with thermal conductivity and inversely with thermal expansion. The validity of these correlations is evaluated for mixed rare earth silicates to determine whether rule of mixtures suffices or other relationships govern behavior. Efforts to find additional iterative feedback between the collaborators are ongoing. Eighteen papers have already been published that illustrate this collaboration.



Technical Progress

Due to the many competing phases in the rare earth disilicate systems, predicting the formation of high-entropy single phases from first-principles is computationally challenging. We are currently training machine-learning models to predict phase formation on a combination of experimental and computational data. Initial models based on decision trees indicate that important features include the mean and standard deviation of ionic radii. We are currently calculating formation enthalpies for all of the component phases to enlarge the feature set.

Neutron pair distribution function analysis reveals that $Yb_2Si_2O_7$ has triclinic symmetry in the short range while $Er_2Si_2O_7$ has monoclinic symmetry. The local triclinic structure is hypothesized to lead to the rotation of the thermal expansion principal axes in $Yb_2Si_2O_7$ and other rare earth disilicates that exhibit rotation.

Sol-gel synthesis of phase-pure rare earth disilicates requires control of the hydrolysis reaction of silica. This is facilitated by low pH chemistries with the only water needed for hydrolysis provided by the rare-earth nitrate precursors. A triclinic phase was observed to nucleate for $Yb_2Si_2O_7$, $Er_2Si_2O_7$, and $Y_2Si_2O_7$ prior to converting to

the equilibrium monoclinic phase. The phase transformation is accompanied by a 10% volume change, which may be problematic for mechanical integrity of coatings made by this synthesis route.

Melting temperatures of single RE mono- and di-silicates were determined via laser melting, and monitoring the temperature of thermal arrests on cooling using a spectropyrometer. Finally, periodic trends for CMAS interactions with individual and multicomponent REMS are explained by the varying dissolution and thermodynamic stability of precipitated RE silicate apatite phases.

Future Plans

In the final year, we will continue to work on training machine-learning models to directly predict phase formation in multi-component rare-earth disilicates. The formation enthalpies will be calculated using DFT and corrected using the coordination-corrected enthalpies approach. The minimum, maximum, mean and standard deviations of the corrected formation enthalpies for the sets of single-component disilicates for each composition will be added to the feature vector, and used to train improved machine-learning models. Once the new feature vectors have been generated, they will also be used to train machine-learning models based on different methods, including gradient boosted decision trees, random forests, neural networks, and Gaussian processes. Gaussian processes are particularly useful when dealing with small data sets, as they can give an uncertainty associated with the predictions. This can then be used to identify new compositions that can be tested in an effort to improve the accuracy of the model predictions. Finally, we will attempt to train models to try to predict the structural phase most likely to be formed by a composition, and not just whether it will form a single-phase or multiple phases.

Broader Impacts and Workforce Development

Throughout this project, efforts have been made to educate, disseminate the methods and results of this effort. Multiple online AFLOW workshop tutorials have been offered to train current and future users in the operation of the AFLOW software and its associated APIs and data access tools. Eighteen papers have already been published with additional publications planned. More than 20 seminars, conference presentations, webinars have been given related to this collaboration. At least three postdoctoral associates/research scientists, thirteen graduate students have been sponsored by this project. Many have graduated and now have positions at government institutions such as Oak Ridge National Lab, Naval Research Lab, Nuclear Regulatory Commission, as well as at small companies and academic institutions.

Data Management and Open Access

All the results of this study are made available via FAIR (findable, accessible, interoperable, reusable) practices. Computational data generated in this project are made available through the aflow.org web portal, and using the AFLOW REST-API and AFLUX Search-API.
Experimental data are made available on UVA's Libradata system, for example:
https://dataverse.lib.virginia.edu/dataset.xhtml?persistentId=doi:10.18130/V3/XI7QGF
Dissertations are made available on UVA's Libra system, for example:
https://libraetd.lib.virginia.edu/public_view/x920fx56f.

Advancing Along the Materials Development Continuum and Partnerships to Translation

This project accelerates materials discovery and development over trial and error, empirical experimental studies which would otherwise be required for compositions utilizing optimized combinations of the eighteen rare earth elements in rare earth mono- or di-silicates. The project's outputs are most likely to be adopted, integrated, or deployed into high temperature coatings intended for application in hot-section turbine engines. The open-access databases developed and made available via AFLOW enable wide adaptation. This project is funded as a Grant Opportunities for Academic Liaison with Industry (GOALI), enabling rapid adaptation of results by Rolls-Royce Corporation. Rolls-Royce has recently translated SiC-based ceramic composites with rare earth silicate coatings from materials research to engine development status. The promise of "high-entropy" rare earth silicates as coatings for ceramic composites has been translated to an ARPA-E-funded project of "high-entropy" rare earth oxide RE_2O_3 "HERO" coatings for refractory alloys that have higher thermal expansion than SiC-based ceramic composites.

Publications

1. C. M. Rost, T. Borman, M. D. Hossain, M. Lim, K. F. Quiambao-Tomko, J. A. Tomko, D. W. Brenner, J.-P. Maria, and P. E. Hopkins. *Electron and phonon thermal conductivity in high entropy carbides with variable carbon content*. Acta Materialia, **196**, 231–239 (2020). https://doi.org/10.1016/j.actamat.2020.06.005
2. Z. Ding, M. Ridley, J. Deijkers, N. Liu, M. S. B. Hoque, J. Gaskins, M. Zebarjadi, P. Hopkins, H. Wadley, E. Opila, and K. Esfarjani. *The thermal and mechanical properties of hafnium orthosilicate: Experiments and first-principles calculations.* Materialia, **12**, 100793 (2020). https://doi.org/10.1016/j.mtla.2020.100793
3. D. H. Olson, V. A. Avincola, C. G. Parker, J. L. Braun, J. T. Gaskins, J. A. Tomko, E. J. Opila, and P. E. Hopkins. *Anisotropic thermal conductivity tensor of β-$Y_2Si_2O_7$ for orientational control of heat flow on micrometer scales.* Acta Materialia, **189**, 299–305 (2020). https://doi.org/10.1016/j.actamat.2020.02.040
4. R. Friedrich, M. Esters, C. Oses, S. Ki, M. J. Brenner, D. Hicks, M. J. Mehl, C. Toher, and S. Curtarolo, *Automated coordination corrected enthalpies with AFLOW-CCE*, Phys. Rev. Mater. **5**, 043803 (2020). https://doi.org/10.1103/PhysRevMaterials.5.043803
5. D. Hicks, M. J. Mehl, M. Esters, C. Oses, O. Levy, G. L. W. Hart, C. Toher and S. Curtarolo, *The AFLOW Library of Crystallographic Prototypes: Part 3*, Comput. Mater. Sci. **199**, 110450 (2021). https://doi.org/10.1016/j.commatsci.2021.110450
6. G. L. W. Hart, T. Mueller, C. Toher and S. Curtarolo, *Machine learning for alloys*, Nat. Rev. Mater. **6**, 730 (2021). https://doi.org/10.1038/ s41578-021-00340-w
7. C.W. Andersen, R. Armiento, E. Blokhin, G.J. Conduit, S. Dwaraknath, M.L. Evans, Á. Fekete, A. Gopakumar, S. Gražulis, A. Merkys, F. Mohamed, C. Oses, G. Pizzi, G.-M. Rignanese, M. Scheidgen, L. Talirz, C. Toher, D. Winston, et al., *OPTIMADE: an API for exchanging materials data*, Sci. Data **8**, 217 (2021). https://doi.org/10.1038/s41597-021-00974-z
8. D. H. Olson, J. A. Deijkers, K. Quiambao-Tomko, J. T. Gaskins, B. T. Richards, E. J. Opila, P. E. Hopkins, H. N. G. Wadley, *Evolution of microstructure and thermal conductivity of multifunctional environmental barrier coating systems*, Materials Today Physics **17**, 100304 (2021). https://doi.org/10.1016/j.mtphys.2020.100304
9. M.J. Ridley, E.J. Opila, *Quantitative Evaluation of (0001) Sapphire Recession in High-Temperature High-Velocity Steamjet Exposures*, Journal of the European Ceramic Society **42**, 631-7 (2022). https://doi.org/10.1016/j.jeurceramsoc.2021.07.064
10. H. J. Kulik, T.Hammerschmidt, J. Schmidt, S. Botti, M. A. L. Marques, M. Boley, M. Scheffler, M. Todorovic, P. Rinke, C. Oses, A. Smolyanyuk, S. Curtarolo, A. Tkatchenko, A. P. Bartók, S. Manzhos, M. Ihara, T. Carrington, J. Behler, O. Isayev, M. Veit, A. Grisafi, J. Nigam, M. Ceriotti, K. T. Schütt, J. Westermayr, M. Gastegger, R. J. Maurer, B. Kalita, K. Burke, R. Nagai, R. Akashi, O. Sugino, J. Hermann, F. Nóe, S. Pilati, C. Draxl, M. Kuban, S. Rigamonti, M. Scheidgen, M. Esters, D. Hicks, C. Toher, P. V. Balachandran, I. Tamblyn, S. Whitelam, C. Bellinger, and L. M. Ghiringhelli, *Machine Learning in Electronic Structure*, Electronic Structure **4**, 023004 (2022). https://doi: 10.1088/2516-1075/ac572f
11. C. Toher, C. Oses, M. Esters, D. Hicks, G. N. Kotsonis, C. M. Rost, D. W. Brenner, J.-P. Maria, and S. Curtarolo, *High-entropy ceramics: propelling applications through disorder*, MRS Bull. **47**, 194-202 (2022). https://doi: 10.1557/s43577-022-00281-x
12. M. Esters, C. Oses, D. Hicks, M. J. Mehl, M. Jahnàtek, M. D. Hossain, J.-P. Maria, D. W. Brenner, C. Toher, and S. Curtarolo, *Settling the matter of the role of vibrations in the stability of high-entropy carbides*, Nat. Commun. **12**, 5747 (2021). https://doi: 10.1038/s41467-021-25979-5
13. M.J. Ridley, K.Q. Tomko, J.A. Tomko, E.R. Hoglund, J.M. Howe, P.E. Hopkins, E.J. Opila, *Tailoring Thermal and Chemical Properties of a Multi-component Environmental Barrier Coating Candidate ($Sc_{0.2}Nd_{0.2}Er_{0.2}Yb_{0.2}Lu_{0.2})_2Si_2O_7$*. Materialia, **26**, 101557 (2022). https://doi.org/10.1016/j.mtla.2022.101557
14. M. Ridley, E. Opila, *Variable thermochemical stability of $RE_2Si_2O_7$ (RE = Sc, Nd, Er, Yb, or Lu) in high-temperature high-velocity steam*, Journal of the American Ceramic Society **105**, 1330-1342 (2022). https://doi.org/10.1111/jace.18120
15. P.E. Hopkins, J.A. Tomko, A. Giri, *Quasi-harmonic theory for phonon thermal boundary conductance at high temperatures*, Journal of Applied Physics **131**, 015101 (2022). https://doi.org/10.1063/5.0071429
16. C. Toher, M. J. Ridley, K. Q. Tomko, D. H. Olson, S. Curtarolo, P. E. Hopkins, and E. J. Opila. *Design rules for the thermal and elastic properties of rare-earth disilicates*. Materialia, **28**, 101729 (2023). https://doi.org/10.1016/j.mtla.2023.101729
17. A. Salanova, I.A. Brummel, A.A. Yakovenko, E.J. Opila, J.F. Ihlefeld, *Phase stability and tensorial thermal expansion properties of single to high-entropy rare-earth disilicates*. Journal of the American Ceramic Society, **106**, 3228-3238 (2023). https://doi: 10.1111/jace.18986

18. A. Salanova, E.J. Opila, J.F. Ihlefeld. *Phase purity and evolution in sol–gel derived single component and multicomponent rare-earth disilicates.* Journal of the American Ceramic Society **107**, 3687-3700 (2024). https://doi: 10.1111/jace.19672

The Materials Project

Kristin Persson

The vision of the Materials Project (materialsproject.org/) is to leverage the continuing developments in materials theory to compute many of the basic properties of all known materials and beyond, in order to a) rapidly screen for novel materials with interesting properties; b) accelerate the development of quantitative higher length scale models; and c) form a well-tested and curated dataset on which to develop and test machine learning and materials informatics methods to extract insights. In parallel, we demonstrate how such an information-driven approach serves the materials research community and accelerates materials design. Within the BES-MSE core program, we apply our approach on novel functional electronic compounds, alloy systems and interfaces exhibiting magnetic, elastic and/or electric coupling, and topological materials – which provide foundational support to several DOE BES priority research areas including e.g. Liquid Solar Fuels, Microelectronics, QIS and Artificial Intelligence and Machine Learning.

Spin Dynamics and Transport Properties of solids from Ab-initio Density-Matrix Dynamics (ADEPTS)

Lead Investigator: Yuan Ping, yping3@wisc.edu
Participating Institutions: University of Wisconsin-Madison, Rensselaer Polytechnic Institute
Source of Support: DOE-BES
Website: https://adepts.engr.wisc.edu/
Keywords: computation, quantum dynamics, quantum materials, spintronics, quantum information science

Abstract: Ab initio spin dynamics and transport simulations are critical for predicting new materials and realizing the potential of spintronics, spin-based quantum information science, and spin-selective photo-chemistry. In particular, simulations would be invaluable to predict key physical parameters including spin lifetime, spin diffusion and coherence length, magneto-optical spectra, and (spin)-photocurrent. In this presentation we will introduce our recently developed real-time density-matrix dynamics approach with first-principles electron-electron, electron-phonon, electron-impurity scatterings and self-consistent spin-orbit coupling. We are developing a computational framework and an open-source implementation targeting exascale GPU-based computing resources for simulating spatio-temporal quantum dynamics and transport accounting for a range of quantum degrees of freedom (e.g., charge, spin, orbital, lattice) in arbitrary device geometries. We leverage exascale computing capabilities to pioneer the simulation of spin and charge dynamics and transport, from DC to terahertz, in disparate materials with arbitrary geometry up to micrometer length scales, which is essential to study complex chemical systems.
We show our methods can accurately predict spin and carrier lifetime, spin diffusion length, and pump-probe Kerr-rotation signatures for general solids, with examples of Si, GaAs, 2D materials, and halide perovskites. We show our recent study of how g factor fluctuations lead to spin dephasing in halide perovskites under external magnetic recent progress of developing methodology for spin-optotronic signatures, such as circular dichroism and circular/spin photogalvanic effect to chiral and broken-inversion-symmetry solids. Importantly, with our real-time density matrix dynamics, we can explicitly include excitation, scattering, simulated and spontaneous emission processes from ab-initio calculations (a full quantum kinetics formalism), at presence of quantum scatterings. Such formalism can also be applied to computing various transient and steady-state photocurrents or nonlinear optics. Finally, we will present initial results on accurate ab-initio prediction of spin diffusion length in graphene and related systems. We show that materials with a unique symmetry and spin-orbit coupling, in which a Persistent Spin Helix occurs, are immune to the dephasing from different path length in spatial transport. Our results provide important insights for spin-optotronic properties and spin transport in chiral or non-centrosymmetric systems.

Project Scope

We propose to develop a fully general, massively parallel computational platform for first-principles quantum dynamics and transport with a density-matrix formalism with both coherent and incoherent dynamics of spin, electrons, phonons and photons. We will develop our tools for both optical and X-ray probes with circular polarization in ultrafast dynamics, and include spatial inhomogeneity for quantum transport. In this program, we will have a particular focus on developing tools for simulating spin and spin-orbit related photochemistry through controlling optical orientation and chirality of materials - a rising field of "Spin Chemistry". We then simulate spin-selective excited electron generation, relaxation and decoherence, as well as transport in molecular and hybrid materials, in particular chiral systems, to answer the outstanding questions of fundamental mechanisms on chiral-induced spin selectivity ("CISS" effect) and spin-dependent photocatalysis.

Relevance to MGI

This project will be in close collaboration with experimentalists from SLAC, DOE EFRC CHOISE center and UW-Madison on ultrafast spin dynamics. We will apply our developed computational techniques to predict new materials properties and interpret experimental spectroscopic data. In particular we will form a closed loop between experiments, theory and computation. The data generated from this project will serve important guidelines to experimental synthesis and measurements.

Technical Progress

We developed the methodology in several fronts: 1. Extending our open quantum dynamics methods to complex materials requires the treatment of temperature-dependent phonons due to anharmonic effects. 2. We have developed key components to leverage GPU supercomputers for the entire *ab initio* quantum dynamics pipeline. We have implemented GPU-scalable AIMD in the open-source QimPy software. 3. We have extended our theoretical formulation of open quantum dynamics to treat spatial transport of first-principles density matrices (FPDM) on the same footing. In this formalism, each spatial grid point evolves the previously developed FPDM dynamics treating spin, valley etc. fully generally for any material symmetry or dimensionality, allowing integration of quantum dynamics and transport into a single framework. 4. We implemented both Kubo formula with a finite difference approach at DFT (similar to our circular dichroism implementation),which effectively avoids the Wannierization step. More importantly we have implemented the real-time photocurrent calculations with light absorption, emission, and scattering.

Future Plans

We will implement our existing FPDM quantum dynamics method as the collision integral in this transport framework in order to couple *ab initio* scattering kernels for arbitrary materials into the device simulations. In particular, we will investigate the chiral induced spin selectivity mechanism in our simulations. We will formulate and implement spin photocurrent in our real time density-matrix dynamics framework and use it to discover and characterize novel topological quantum materials' properties.

Broader Impacts and Workforce Development

This project involves close interdisciplinary collaboration between two institutions, facilitated by two hour-long video conference meetings each week. These meetings facilitate close interactions between 4 graduate students and 3 postdocs in the field of chemistry, physics, and materials science, providing broad training in fields they would not have encountered in core research-group projects. The research meetings also provide regular presentation opportunities for students and postdocs, facilitating training for effective dissemination of research results. In Feb. 2023 and Mar. 2024, we organized a 3-day research and code-development workshop which significantly advanced the method formulation and code developments, and facilitated more extensive communications between the members of the two groups.

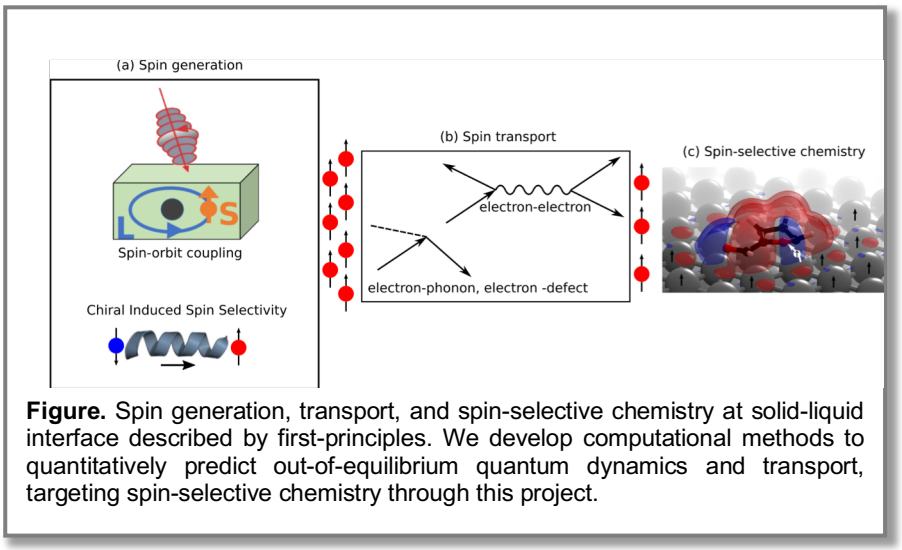


Figure. Spin generation, transport, and spin-selective chemistry at solid-liquid interface described by first-principles. We develop computational methods to quantitatively predict out-of-equilibrium quantum dynamics and transport, targeting spin-selective chemistry through this project.

Data Management and Open Access

All research data generated by this project will be preserved and disseminated through publications and publicly-accessible databases. Importantly, beyond just sharing data with the research community, we will emphasize all aspects of FAIR (Findability, Accessibility, Interoperability and Reusability) data principles. Critical to this is the central role of widely-adopted open source codes with standardized and open data formats, which will make all published data reusable by and interoperable with other research efforts. This project will not generate or use Personally Identifiable Information (PII), and any data with national security implications, business confidentiality or intellectual property concerns will not be released in accordance with all laws and DOE regulations, orders, and policies.

Advancing Along the Materials Development Continuum and Partnerships to Translation

N/A

Publications and References

1. **"**How Spin Relaxes and Dephases in Bulk Halide Perovskites"**,** Junqing Xu†, Kejun Li†, Uyen N. Huynh, Jinsong Huang, Ravishankar Sundararaman*, Valy Vardeny*, and Yuan Ping***,** *Nature Communications*, 15, 188, (2024).
2. "Circular Dichroism of Crystals from First Principles**"**, Christian Multunas, Andrew Grieder, Junqing Xu**,** Yuan Ping*, Ravishankar Sundararaman*, *Physical Review Materials*, 7, 123801, (2023)

Collaborative Research: DMREF: Transforming Photonics and Electronics with Digital Alloy Materials

Lead Investigator: Viktor Podolskiy (viktor_podolskiy@uml.edu), Evgenii Narimanov, Daniel Wasserman, Seth Bank, Avik Ghosh
Participating Institutions: University of Massachusetts Lowell, Purdue University, University of Texas at Ausitn, University of Virginia.
Source of Support: NSF-DMREF, AFRL.
Keywords: Metamaterials, Nonlocal Electromagnetism, Semiconductors, Digital Alloys

Project Scope

We consider the implications of optical hyperbolic response, that is known to enable sub-diffraction light compression, combined with engineered electronic response in a new class of digital alloy materials, for new frontiers in photonics and electronics.

Relevance to MGI

The team includes experts in "pen and paper" theory, computations, and experiments. The team works together, iterating the experimental designs around the theoretical predictions. Together, we are exploring a fundamentally new regime of light-matter interaction, designer nonlocal electromagnetism, where simultaneous confinement of optical light and engineering of charge movement can yield novel electromagnetic materials, materials where polarization field at a given point depends on electric field at a different point. Electromagnetic response of such materials would deviate from predictions of "textbook" local Maxwell equations, opening new directions for opto-electronics. In less than two years, we already have developed theoretical framework that qualitatively describes electromagnetic response, and experimentally verified existence of optical nonlocalities. We are in the process of fine-tuning numerical models that would quantitatively describe light-matter interaction in our materials.

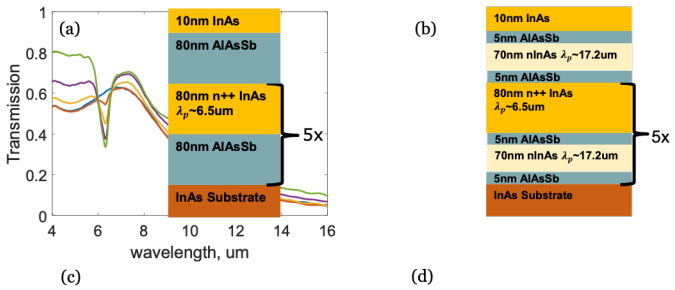


Figure. Please Experimental (a,b) and theoretical (c,d) transmission spectra of local (a,c) and nonlocal (b,d) semiconductor metamaterials. Insets in top figures illustrate material composition. Nonlocality results in additional transmission minima

Technical Progress

Previous studies of hyperbolic metamaterials primarily considered binary layered composites comprising doped (plasmonic) layers whose electromagnetic response is dominated by the dynamics of the free charges, and dielectric "barrier" layers. While optical response of plasma is known to be nonlocal, the presence of barriers prevented observation of nonlocal electrodynamics in bi-layer composites. We have also considered transition of optical signatures of bi-layered materials in the regime where plasmonic layers

become increasingly thinner, confining, and eventually quantizing electromagnetic response of free charges, demonstrating emergence of ballistic resonances.

In this work we explore fundamentally new regime where homogeneous barrier layers are replaced with engineered multi-layered structures, enabling tunneling of charges between neighboring plasmonic layers, and thereby enabling strongly nonlocal optical response – while preserving optical hyperbolicity. We have explored the transition between local and nonlocal electromagnetism experimentally and developed theoretical understanding of the underlying processes. We are in process of fine-tuning first-principles calculations aiming for quantitative description of the phenomena.

Future Plans

As mentioned above, we are currently working on developing a first-principles-based description of the underlying optical response. In parallel, we are using our theoretical framework to understand non-monochromatic behavior of light in our nonlocal media, including propagation of ultrafast pulses and analyzing the potential for using our material for ultrafast pulse-shaping at mid-infrared frequencies.

Broader Impacts and Workforce Development

The students involved in the project obtain unique convergent training in all aspects of materials science, from solid state theory, to electromagnetism, to computational materials science, to molecular beam epitaxy, to characterization, to data analysis. The geographically diverse team holds bi-weekly zoom progress meetings where students typically report on their progress, with (when needed) faculty advisors putting individual pieces of the puzzle together. We are planning the visit of UML students to UT to learn first-hand skills with experiments and to illustrate our theory tools to our experimental colleagues.

Data Management and Open Access

When the manuscripts get published, the relevant numerical codes are deposited to GitHub (see, e.g. https://github.com/viktor-podolskiy), with relevant characterization data added as supplementary materials.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Our team is working on semiconductor materials that are “workhouses” of infrared electro-optics. We envision that the novel materials that are designed in the course of our project will be integrated in this existing pipeline and will be readily transitioned to the commercial sector. We are collaborating with our partners at AFRL on exploring the opportunities of our new materials for AFRL needs

Publications and References

1. Y. Huang, H. Tang, B. Zheng, Y. Dong, M. Haerinia, V. A. Podolskiy, and H. Zhang, "*Inverse Design of Photonic Structures Using Automatic Differentiable Rigorous Diffraction Interface Theory*," in *CLEO 2023*, Technical Digest Series (Optica Publishing Group, 2023), paper JTu2A.119
2. E. Narimanov, *Insurgent Metamaterials: light transmission by forbidden transitions*, arXiv:2310.05434 (2023)
3. Y. Huang, Z. Zhu, Y. Dong, H. Tang, B. Zheng, V.A. Podolskiy, H. Zhang, *Eigendecomposition-free inverse design of meta-optics devices*, Optics Express, **32**, 13986 (2024)

DMREF: Computational Chemistry to Accelerate Development of Long Wave Infrared Polymers

Lead Investigator: Jeffrey Pyun, University of Arizona (all Co-PIs at UArizona)
Participating Institutions: AFRL
Website: *https://live-azs-dmref-lwir.pantheonsite.io/*
Keywords: infrared optics, infrared spectroscopy, optical polymers, machine learning

Project Scope

We propose to develop ***a new class of high refractive index, optical polymers*** that will enable the first use of ***low cost, plastic optics for long-wave infrared (LWIR) thermal imaging***. The key to accelerating materials design and optical-element fabrication will be the development of high-throughput computational methods combined with machine learning and the application of an integrated feedback loop with synthesis, processing, and optical characterization.

Relevance to MGI

The key to this advance will be the use of computational chemistry to rapidly simulate the infrared vibrational characteristics of candidate organic molecules, which when copolymerized with elemental sulfur, to enable creation of the desired IR optical polymers. Density functional theory (DFT) and machine learning (ML) will be utilized to create spectral databases from the "bottom up" with candidate molecules of interest that will possess limited vibrational absorption in the LWIR spectrum from 7-14 μm. Understanding the solubility parameters of molten liquid sulfur calls for computational studies on the chemical nature of molten elemental sulfur using molecular dynamics (MD). ***We have developed the first comprehensive training set for viable molecular dynamics simulations of dynamic liquid sulfur and polymeric sulfur processes using reactive force field (ReaxFF) methods*** in collaboration with the van Duin group at Penn State.

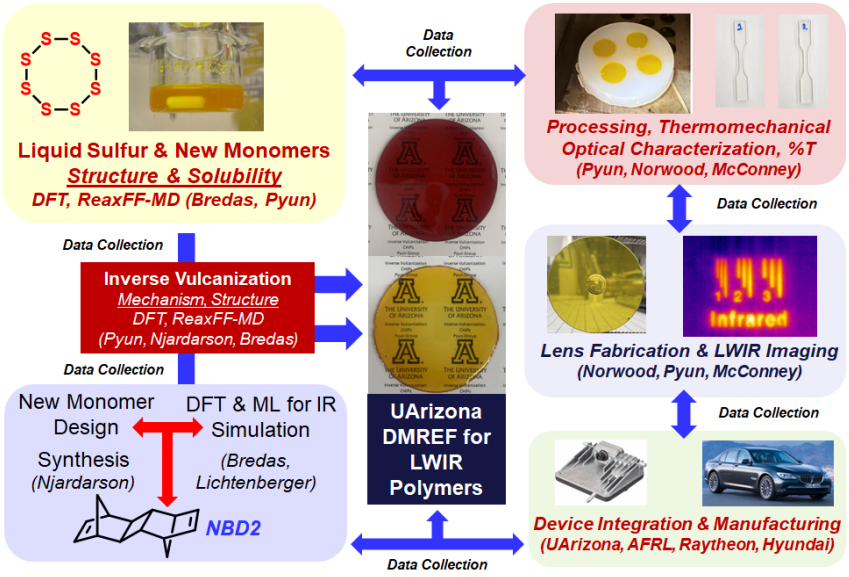


Fig. 1: Proposed research concept using computational chemistry & machine learning to accelerate the materials discovery of the first examples of LWIR polymers as optical components for LWIR thermal imaging.

Technical Progress

1) The **Brédas group** in collaboration with the Van Duin group (Penn State) has developed the first viable reactive force field (ReaxFF) molecular dynamics simulations for the ring-opening polymerization of elemental sulfur. (**Figure 1**). The **Brédas and Lichtenberger groups** have developed and submitted for publication the first report on using DFT calculations for simulating IR vibrational spectra (in terms of both frequencies and intensities) with B3LYP functionals for large libraries of organic molecules (+30,000) along with DFT modeling of conjugated π-systems for LWIR transparency.[1,2]

2) The **Njardarson group** has synthesized over 6 new organic compounds in the past year that include sulfur-richorganophosphorous (dithiophosphoric acids) compounds and cyclic olefins with novel molecular architecture.[3,4] The **Njardarson, Pyun, Brédas, Norwood and AFRL groups** collaborated on the first synthesis of perdeutero styrenic monomers to enable the first comparison of structure-property effects in sulfurated *proteo vs deutero* polymers with respect to IR transparency.[5]
3) The **Pyun group** has led the synthetic and optical fabrication efforts in this DMREF team to prepare new sulfur polymers and fabricate IR plastic optics with these new materials.
4) **The Norwood group** has developed polymer processing and nanofabrication methods for the first time including the fabrication of a LWIR sulfur plastic lenses, along with sulfur polymer integrated photonic devices in the form of polymer waveguides, microring resonators and phase shifted Bragg gratings. **Pyun and Norwood** just submitted the first comprehensive review of IR plastic optics and polymeric integrated photonics with sulfur containing polymers made by inverse vulcanization.[9]

Future Plans

1) ***RexaFF studies on liquid sulfur:*** The **Brédas** group will continue to develop methods and optimize the training sets for the chemical speciation of molten sulfur and for the first time explore the solubility parameter for liquid sulfur.
2) ***New LWIR polymers from inverse vulcanization:*** The **Njardarson and Pyun groups** will continue the synthesis of new candidate molecules, an effort that has already demonstrated a five-fold increase in new candidate monomers that have been screened for inverse vulcanization. The deployment of a new family of norbornadiene-based sulfur polymers is anticipated for Yr-4.
3) ***Prototype LWIR imaging systems and LWIR imaging standards:*** The **Norwood** group will create a true broadband visible-NIR-SWIR-MWIR-LWIR sulfur plastic lens based on a new Frensel lens design incorporating broadband diffractive elements and demonstrate the benefits of the full spectrum optical transparency unique to sulfur polymers that cannot be achieved with state-of the-art inorganic IR optical materials.

Broader Impacts and Workforce Development

The UArizona DMREF team is strongly committed to the professional training of researchers on the project with strong industrial mentoring from Gerald Uyeno (Engineering Fellow, Raytheon Missile System, Tucson, AZ) and partnerships with AFRL through the McConney group. From a training standpoint, the computational aspects of the project are led by two women research scientists (Dr. Eunkyung Cho, Dr. Maliheh Tameh) and currently supports three women graduate students from the Pyun (Lindsey Holmen, Katie Martin) and Norwood (Kate Newcomer) groups. In 2023, an ambitious new undergraduate mentoring effort over 20 UArizona undergraduates are mentored EVERY SEMESTER with a total exceeding 50 students by the end of Spring 2024.

Data Management and Open Access

New digital data and software for the T3ML tool are still being developed, so broader dissemination of this digital output is pending for 2024. We anticipate initially filing new IP on this software, followed by initial disclosure of results and data through publication in peer-reviewed scientific journals. Posting of IR databases for use by the general public on the UArizona DMREF site is planned for Fall 2024 and linked to the NIST IR databases per future coordination.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The UArizona DMREF team is well-positioned for industrial engagement and translation of the work from this project with leading IR camera OEM's through NSF I-Corps. UArizona has a strong IP position on new optical materials through support of new IP by the State of Arizona through the UArizona technology transfer office, TechLaunch Arizona (TLA). Furthermore, the UArizona DMREF team has existing projects, or collaborations with multi-national companies from the optical and defense industrial sectors (PPG, LG CHEM, MOBASE, Raytheon, Hoya).

Publications and References

(**1**) Cho, E.; Pratik, S. M.; Pyun, J.; Coropceanu, V.; Bredas, J.-L. *Adv. Opt. Mater.* **2023**, *(12), 2300029.*
(**2**) Tameh, M. S.; Coropceanu, V.; Pyun, J.; Lichtenberger, D. L. Brédas, J. L. *ACS Materials Letters* **2024***, submitted*.
(**3**) Marshall, C.E.; Molineux, J.; Kang, K.; Kim, K.; Norwood, R.A.; Njardarson, J. T.; Pyun, J. *JACS* **2024,** *submitted*.
(**4**) Bao, J.; Kang, K.; Molineux, J.; Bischoff, D.J.; Mackay, M. E.; Pyun, J.; Njardarson, J. T. *Angew. Chem. Int. Ed.* **2024,** 63, e202315963.
(**5**) Qureshi, M. H.; Bao, J.; Kleine, T. S.; Kim, K.-J.; Carothers, K. J.; Molineux, J.; Cho, E.; Kang, K.-S.; Godman, N. P.; Coropceanu, V.; Bredas, J. L.; Norwood, R. A.; Njardarson, J.; Pyun, J.; *JACS* **2023**, *145,* 27821–27829.
(**6**) Nishant, A.; Kim, K.; Himmelhuber, R.; Lee, T.; Kleine, T. S.; Pyun, J.; Norwood, R. A. *Adv. Opt. Mater.* **2024**, *submitted*.
(**7**) Molineux, J.; Lee, T.; Kim, K.; Nishant, A.; Kleine, T. S.; Lyons, N. P., Durfee, S.; Norwood, R. A.; Pyun, J. *Adv. Opt.. Mater.* **2024**, *12*, 2301971.
(**8**) Arough, S.; Nishant, A.; Pyun, J.; Norwood, R. A.; *Optics Materials Express* **2023**, *13,* 2737-2745.
(**9**) Pyun, J.; Norwood, R .A.; *Prog. Polym. Sci*. **2024** *under revision.*
(**10**) Bao, J.; Martin, K. P.; Kang, K.; Cho, E.; Bredas, J.-L; Glass, R. S.; Parker, W. O.; Njardarson, Pyun, J. *JACS* **2023**, *145*, 12386–12397.

Collaborative Research: DMREF: Active Learning-based Material Discovery for 3D Printed Solids with Heterogeneous Electrical and Mechanical Properties

Lead Investigator: H. Jerry Qi, qih@me.gatech.edu
Participating Institutions: Georgia Institute of Technology, Florida International University
Source of Support: NSF-DMREF
Website: none
Keywords: Active learning; additive manufacturing; 3D printing; conductivity; heterogeneous properties.

Project Scope

This proposed work is to establish an active learning (AL) approach for discovering resins composed of different monomers suitable for vat photopolymerization additive manufacturing of robust materials wherein the conductivity can be locally controlled from conductive to non-conductive.

Relevance to MGI

Additive manufacturing (AM; or 3D printing) has seen exponential growth in recent years. One emerging area is to use AM for functional devices, such as sensors. However, the current AM techniques face challenges for fabricating functional devices due to the lack of multimaterial capability. Grayscale digital light processing (g-DLP), where light intensity (grayscale) controls the local mechanical properties within a monolithic part, has shown promising potential. PI group also explored g-DLP printing conductive structures for functional devices. To further expand the field, more resins should be developed. However, due to the large number of available monomers and the large range of material properties, resin development is a significant challenge. This research will develop advanced multi-task active learning approaches to discover monomers for g-DLP printing where the conductivity of the printed part can be locally controlled from conductive to non-conductive. The active learning (AL) loop begins by training machine learning (ML) models on experimental data of material properties and their standard deviations. The ML models then suggest new compositions that have the largest potential to improve the prediction accuracy. New experiments are conducted to validate and train ML models. This loop will continue until the ML models can give accurate predictions.

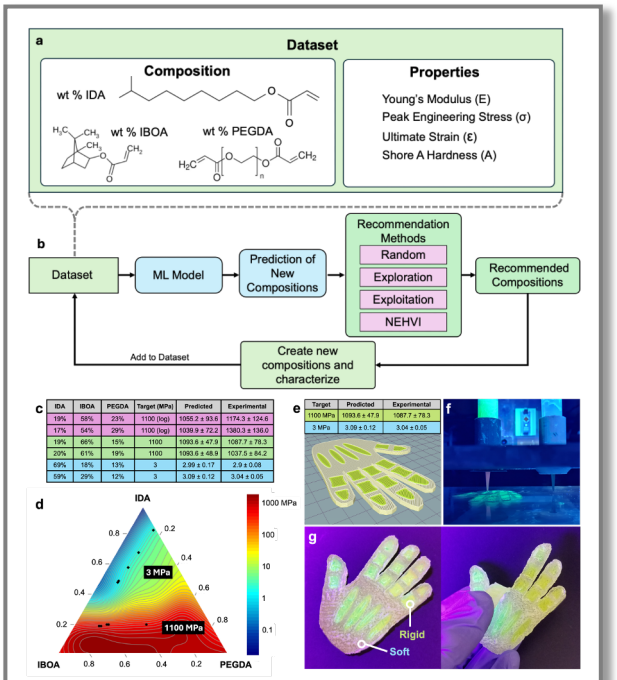


Figure. Active learning (AL) for the discovery of 3D printable photopolymers with targeted properties. a) Three monomers were used and the targeted properties. b) The process of active learning. c) Resin compositions suggested the AL to targeted Young's moduli of 1100MPA and 3MPa. d) The locations of these compositions in modulus chart. e,g) A 3D printed hand with soft (skin) and hard (bone) regions.

Technical Progress

Since the start of this project in October 2023, our team has made some significant progresses.

First, we have developed an AL approach to efficiently recommend multi-monomer resins to provide desired materials properties (also see **Figure**). Our method seeks to build an accurate predictive model while minimizing the number of experiments required to explore a composition space for targeted materials design. To test our approach, we select a design space consisting of three free radical polymerizing monomers (Figure a) ranging from rigid to elastomeric. The properties of interest are Young's Modulus (E), peak engineering stress (σ), ultimate strain

(ε), and Shore A hardness. Our AL approach detailed in Figure b begins with an initial training dataset, which are used to train a Gaussian Process Regression (GPR) model. The GPR model is used to predict the specified material characteristics of all possible monomer compositions in the design space (Section 2.2). Next, we use Noisy Expected Hypervolume Improvement (NEHVI) model to select several high-quality compositions to synthesize and characterize. The selected compositions are then added to the dataset, and the cycle is repeated for five iterations, followed by a final uncertainty-based exploration selection to preclude regional inconsistencies. Moreover, we demonstrate the ability to accurately predict and subsequently recommend monomer compositions using fine-tuned hierarchical ML models and an exploitation recommendation (Figure c,d). This method recommends compositions with desired numerical values of Young's moduli within 10% accuracy. Finally, we demonstrate a potential application of this technique to additive manufacturing through the multi-material fabrication of a hand with "skin" and "bones." (Figure e-g). This work confirms our assumption in our proposal that active learning is a promising method to explore a multi-monomer design space, revealing new materials that can satisfy a breadth of applications. One paper is published in ACS Applied Materials & Interfaces[1].

Second, we made significant progress in developing the first 3D printable resin where, when lithium salt is added, we can use light intensity to control the conductivity. The conductivity contrast reach about 2000 times, which gives the opportunity of creating conductive traces within a non-conductive body. The print quality is high. We also developed molecular dynamic (MD) simulation models and confirmed the glass transition temperature and conductivity of the thermoset polymers that are cured at different degree of conversion. This work confirms our proposed hypothesis and paves the road to expand our active learning approach to discover new resins with heterogeneous mechanical and conductive properties.

Future Plans

We have formed our research team, including recruiting students and have started our monthly meeting. The team work collaboratively. Our future plan is to

- Conduct nanoindentation experiments to detect mechanical properties at high throughput.
- Conduct Raman spectroscopy experiments for molecular compositional analysis.
- Conduct NEXAFS experiments to verify ion transport in polymers at different degrees of conversion.
- Expand monomer selections and improve mechanical properties whilst maintaining conductivity contrast.
- Develop the automated resin deposition and testing system for high throughput material development.
- Integrate the automated resin testing system into the active learning loop.

Broader Impacts and Workforce Development

Our team has recruited five Ph.D. students, including two female students. Additionally, two Ph.D. students in Qi's group participated GT's ENGAGES starting this summer. Each of them is paired with a high school student from underrepresented groups. These two students will work in Qi's group for two years.

Data Management and Open Access

Since the start of this project, our team has generated a significant amount of data. These data are stored in https://github.com/Ramprasad-Group/polyVERSE/tree/main/Other/Thermoset_DMREF_Project maintained by Ramprasad group. We also developed protocols to pass data to Ramprasad group. For example, resins developed in Qi group (including failed ones) were sent to Ramprasad group and stored in the github.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Our work during the first ten months of the project has confirmed two important hypotheses in our proposal: active learning can accelerate the development of thermosetting polymers for 3D printing and local conductive properties in thermosetting polymers can be controlled by light intensity. Currently, we are also working on investigating several high throughput property testing methods, developing an automated polymer synthesis lab, including the automated lab into the active learning loop. We envision these efforts will create an automated polymer discovery system that can accelerate the development of new polymers with a variety of applications.

Publications and References

1. A. Jain, C.D. Armstrong, V.R. Joseph, R. Ramprasad, H.J. Qi, Machine-Guided Discovery of Acrylate Photopolymer Compositions, ACS Applied Materials & Interfaces 16, 17992-18000 (2024). DOI: 10.1021/acsami.4c00759
2. F. Gholami, L. Yue M. Li, A. Jain, A. Mahmood, M. Fratarcangeli, R. Ramprasad, H. J. Qi, Fast and Efficient Fabrication of Functional Electronics Through Grayscale Digital Light Processing 3D Printing. Submitted.

AI-enabled Automated Design of Ultrastrong and Ultraelastic Metallic Alloys

Lead Investigator: Liang Qi, qiliang@umich.edu
Participating Institutions: University of Michigan, Arizona State University, University of North Texas
Source of Support: NSF-DMREF
Website: None
Keywords: AI-enabled automated research workflow, ultrastrong and ultraelastic, complex concentrated alloys, dislocations, local lattice distortions and chemical composition fluctuations,

Project Scope

The project objective is to develop an AI-enabled automated research workflow (ARW) to revolutionize the design and manufacturing of metallic alloys with ultra-high yield strengths and elastic limits. We focus on single-BCC-phase complex concentrated alloys (CCAs) that contain refractory metals. A two-stage ARW transitioning from a data-driven approach to a physics-based one will be constructed to identify and integrate the critical features from each step of materials design (computations, syntheses, characterizations, and testing) to achieve the objective efficiently. The hypothesis is that manipulating local lattice distortions and composition fluctuations can increase the critical stress/strain to move dislocations.

Relevance to MGI

To align with MGI, the two-stage ARW will incorporate electronic/atomistic structure features identified through AI techniques derived from each step of materials design. The first-stage ARW is to train and apply surrogate models to guide synthesis experiments for the initial screening of ultrastrong/ultraelastic alloy candidates, which then will be synthesized combined with in-situ characterization feedback, followed by comprehensive mechanical and structural characterizations using advanced nanomechanical measurements, spectroscopic techniques, and cutting-edge electron microscopy. Statistical methods on dimensionality reduction and feature learning will be applied to extract key features from simulations and characterization results. These key features facilitate the construction of the second-stage physics-based ARW, where Monte Carlo-based simulations will be performed to produce representative structures to describe lattice distortions and local chemical concentration fluctuations. The stochastic dislocation model to predict the critical stress/strain will be derived based on atomistic simulations to advance the knowledge of plastic deformation initiation in CCAs. This physics-based ARW will be used to fine-tune compositions and processing parameters to accelerate alloy design & development.

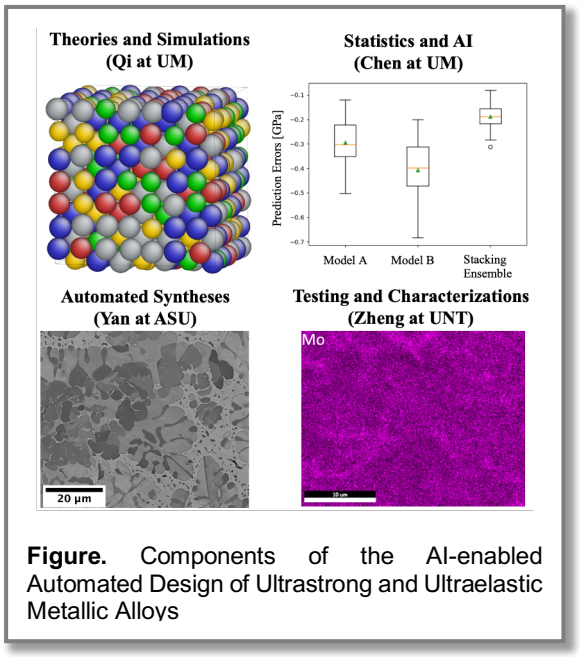


Figure. Components of the AI-enabled Automated Design of Ultrastrong and Ultraelastic Metallic Alloys

Technical Progress

We utilized existing machine learning (ML) surrogate models, including those from the PI's group, to predict the yield strengths and mechanical properties of multicomponent refractory alloy systems. Co-PI Yang Chen at the University of Michigan (UM) collaborated with the PI to analyze the results and enhance these models with improved statistical methods. We then used these ML models to identify non-equimolar alloys with the potential for maximum strength through enhanced lattice distortions. The results were sent to Co-PI Yan at Arizona State University (ASU) for synthesis. Additionally, atomistic simulations were conducted to investigate dislocation motion mechanisms in multicomponent alloys. Parameters such as generalized stacking fault energies, Peierls barriers, and nucleation barriers of screw dislocation lines were studied. Hybrid Monte Carlo and Molecular Dynamics simulations generated atomistic structures with short-range ordering (SRO), whose effects on double

kink nucleation barriers were also examined. On experimental perspective, co-PI Yan at Arizona State University (ASU) initiated the synthesis of designed alloys using sputtering, arc melting, and flash alloying. Refractory alloy candidates included Ta-W-Nb-Mo, Ta-W-Nb-Mo-Re, Ta-Mo-Nb, and Ta-Mo-W systems. Synthesis conditions (pressure, temperature, and time) were added to the AI training database, and crystalline structures were analyzed using X-ray diffraction. Samples were then sent to Co-PI Yufeng Zheng at the University of North Texas (UNT) for structural and chemical composition characterization via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). We studied multiscale structural and compositional non-uniformities in BCC refractory CCAs (RCCAs) using various techniques. The first group of samples, WMoNbTa and $W_{10}Mo_{25}Ta_{25}Nb_{40}$ RCCAs, were analyzed to identify structural and compositional non-uniformities, and the impact of Nb content. Microstructures were studied using SEM, TEM, and STEM, and properties were tested with microhardness and nanoindentation techniques. The second group, WMoNbTaRe and WMoNbTa RCCAs, fabricated using flash alloying, focused on the influence of Re and processing methods.

Future Plans

From a computational and statistical standpoint, Qi and Chen will enhance the first-stage ARW using physics-informed surrogate models and refined feature parameters obtained by advanced statistical techniques from atomistic simulations and experimental characterizations. Gaussian-Process (GP) based sequential designs and iterative methods will explore chemical compositions and synthesis parameters for ultra-strong and ultra-elastic alloys efficiently. For the second-stage ARW, refined Monte-Carlo simulations will generate representative structures matching key features from advanced characterizations. Techniques such as hyperdynamics combined with reinforcement learning will investigate long-term dislocation behavior in CCAs under low strain rates. A stochastic dislocation model will be constructed to predict critical stress/strain in CCAs, considering oxygen impurities. From the synthesis and characterization perspective, Yan will develop a high-throughput synthesis strategy based on in-situ and ex-situ characterization feedback to expedite the search for ideal alloy candidates. Zheng will characterize nanoscale structural and compositional non-uniformities using atomic resolution aberration-corrected scanning transmission electron microscopy (STEM) and atom probe tomography (APT). Zheng will also establish a remote-control station at UNT to operate aberration-corrected S/TEM at The Ohio State University's CEMAS, enabling atomic-resolution characterization to determine lattice distortion and solute/impurity distributions using HAADF-STEM and STEM-XEDX techniques.

Broader Impacts and Workforce Development

This project aims to recruit and train four graduate students across various aspects of materials design, including simulations, statistics, syntheses, characterizations, and testing. The project will also provide training opportunities for a diverse group of undergraduate and high school students, preparing them as future workforces in the MGI. For example, Zheng has organized lab tours for local high school students to showcase the advanced materials characterization facilities at the UNT Materials Research Facility. Zheng also offered a summer internship to a local high school student, Ishan Wakade, providing hands-on materials characterization training using a tabletop SEM and facilitating Zoom meetings/discussions with DMREF-funded graduate students.

Data Management and Open Access

We plan to share the data on Materials Commons, which is a data repository and collaboration platform for the metallurgy and material design community. A new project will be initialized on Materials Commons to record and update descriptions for the experimental and computational processes during the whole DMREF project. Data and scripts related to the published papers will be shared through Materials Commons with unique DOIs. Qi and Chen will also share the ML and simulation codes on GitHub after the user-friendly interface is developed.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Ultrastrong and ultraelastic metallic alloys hold substantial potential for transforming advanced manufacturing and various industrial sectors. The methodologies developed for achieving ultraelastic properties can be extended to other material systems, enabling the tuning of functional properties through significant elastic strain. The PI and co-PIs are also actively search collaboration opportunities with industrial entities on alloy design and developments.

Publications and References

As this project commenced in September 2023, there have not yet been any publications resulting from it.

The Status and Impact of DOE's Energy Materials Network on Hydrogen Technology

Lead Investigator: Michael Rawlings, mrawlings@tms.org
Participating Institutions: The Minerals, Metals, and Materials Society
Source of Support: DOE-EERE
Website:
https://www.tms.org/portal/PUBLICATIONS/Studies/Energy_Materials_Network__EMN/portal/Publications/Studies/EMN/emnStudy.aspx?hkey=dafbe1c4-ea60-42c0-888b-f33f540f60ea
Keywords: Hydrogen, Clean Energy, Infrastructure, Energy Storage, Sustainability

Project Scope

The Minerals, Metals and Materials Society (TMS) conducted a 20-month science and technology accelerator study on the DOE Energy Materials Network (EMN) to assess the status, impact, and future opportunities of four EMN consortia on hydrogen technology: (1) HydroGEN - Advanced Water Splitting Materials Consortium, (2) Electrocatalysis Consortium (ElectroCat), (3) Hydrogen Materials Advanced Research Consortium (HyMARC), and (4) Hydrogen Materials Consortium (H-Mat). This work is intended to identify areas where materials development is needed to fully realize the potential of a clean hydrogen economy and provide recommendations for improving the U.S. energy infrastructure readiness to incorporate this transformative technology.

Relevance to MGI

High performance materials are critical to innovation across many energy technologies vital to national priorities in clean energy, economic growth, and environmental justice. However, to meet the national targets for a clean power sector by 2035 and a net-zero emissions energy sector by 2050, the traditional 15-20 years-to-market timeframe for materials innovations needs to be accelerated.

As a result, the U.S. Department of Energy (DOE) has established the Energy Materials Network (EMN) as a community-of-practice in state-of-the-art materials research and development (R&D) specifically aimed at advancing clean energy technologies. The network comprises core consortia focused on different high-impact energy technologies, each leveraging world-class capabilities at the DOE's National Laboratories to better integrate all phases of materials R&D, from discovery to scale-up and qualification. These consortia help facilitate stakeholder access to the National Laboratories' capabilities, tools, and expertise to accelerate the clean-energy materials development cycle, and enable U.S. manufacturers to deliver innovative, made-in-America products for achieving our energy and environmental justice goals. Each consortium maintains and operates a data repository with the aim of leveraging a MGI-type approach to integrate experiment, computation, and theoretical data to accelerate the development of the novel materials infrastructure needed to support a clean hydrogen economy.

Technical Progress

To equip the broader hydrogen materials community with the knowledge and resources necessary to fully address the DOE's goals for a clean hydrogen economy, this project aimed to accomplish the following: (1) provide an overview the background and current status of the hydrogen-related EMN consortia; (2) assess the impact of the consortia on progressing the materials infrastructure needed to support a clean hydrogen economy; (3) identify the key materials-related challenges and barriers inhibiting development of this economy; and (4) outline recommended areas of focus to improve the readiness of clean hydrogen technology to become a more integral component of the U.S. energy portfolio.

These objectives were accomplished by assembling a team of 14 internationally renowned experts from various materials backgrounds across government, academia, and industry was assembled to lead this effort. The group's insights were collected during eight (8) separate professionally facilitated two-hour (2 hr), live workshops (held in

September and December 2022) as well as virtually via asynchronous online meetings and homework assignments to address the objectives and goals. During these workshops, the study team discussed and prioritized a wide range of topics including the value proposition for both clean hydrogen and the EMN model, the current materials challenges impeding the hydrogen economy, and recommendations for effective future investment. The outputs from these workshops, along with the outcomes of related discussions and activities, were captured and synthesized into a final report. Moreover, input was obtained from the hydrogen-related EMN consortia leadership teams, as well as several other subject matter experts, through small group interviews and/or independent surveys to assess (1) progress towards measurable impact to date, (2) metrics for consortia to measure and share best practices, (3) remaining challenges/barriers to materials development, and (4) opportunities for future growth. The outputs from these activities have been incorporated into a final report.

Future Plans

The final report has been published and is currently available for free download at www.tms.org/studies.

Broader Impacts and Workforce Development

The foundational MGI-like philosophy of the EMN consortia combined with their wide-reaching collaborative nature organically results in the MGI philosophy being conveyed to a broad range of stakeholders outside the immediate materials and/or hydrogen communities and across various sectors. Moreover, each consortia has impacted the next generation of scientist and engineers through REU programs, PhD projects and the hiring and training of post-docs.

Data Management and Open Access

Each of the EMN consortia maintain and operate a data repository which can be access via their consortia websites. A list of their respective websites can be found at:

https://www.energy.gov/eere/energy-materials-network/energy-materials-network#:~:text=Toward%20this%20end%2C%20the%20U.S.%20Department%20of%20Energy,%28R%26D%29%20specifically%20aimed%20at%20advancing%20clean%20energy%20technologies

Advancing Along the Materials Development Continuum and Partnerships to Translation

As the mission of each EMN consortia is to "accelerate the discovery, development, and deployment of new materials" in their respective fields, they each have established R&D methodologies and industrial partnership to achieve this goal. This report aims to clearly articulate and broadly disseminate (1) the value proposition of a clean hydrogen economy, (2) the mission, capabilities and on-going work at these various consortia, and (3) recommended engagement and collaboration opportunities for academic, government and industrial stakeholders to engage with the EMN consortia to develop, advance and/or adopt innovative materials technologies.

Publications and References

Please see the Reference section of *The Status and Impact of DOE's Energy Materials Network on Hydrogen Technology* final report (available for download at www.tms.org/studies) and/or the various consortia websites for a comprehensive list of relevant publications.

NSF NSF BioPACIFIC Materials Innovation Platform

Materials Innovation Platform: BioPACIFIC MIP
MIP Director: Javier Read de Alaniz, javie@chem.ucsb.edu
MIP Co-Director (or Associate Director): Heather Maynard, maynard@chem.ucla.edu
MGI PI Meeting Participant in 2024: Javier Read de Alaniz, javie@chem.ucsb.edu

Participating Institutions: University of California Santa Barbara and University of California Los Angeles
Source of Support: NSF-DMR 1933487
Website: biopacificmip.org
Keywords: MIP, Bio-based polymers, Data driven discovery, Automated polymerization and synthetic biology

Project Scope
BioPACIFIC MIP operates a state-of-the-art user facility that interfaces automation and high-throughput experimentation with synthetic biology and material synthesis. As a knowledge hub for biomaterials innovation, the BioPACIFIC MIP interconnects four primary components: (1) Open-access Facilities; (2) In-House Research, (3) Knowledge Sharing, and (4) Education and Workforce Development.

BioPACIFIC MIP's in-house research served as a hub for four interconnected research elements: (1) living bioreactors, (2) automated synthetic tools for the production of bio-derived materials, (3) hierarchical computational tools and (4) a state-of-the-art characterization facility to enable determination of structure-property relationships. All in-house research projects are driven by the MGI approach, leveraging the integration of simulation/modeling, synthesis/fabrication, and property characterization.

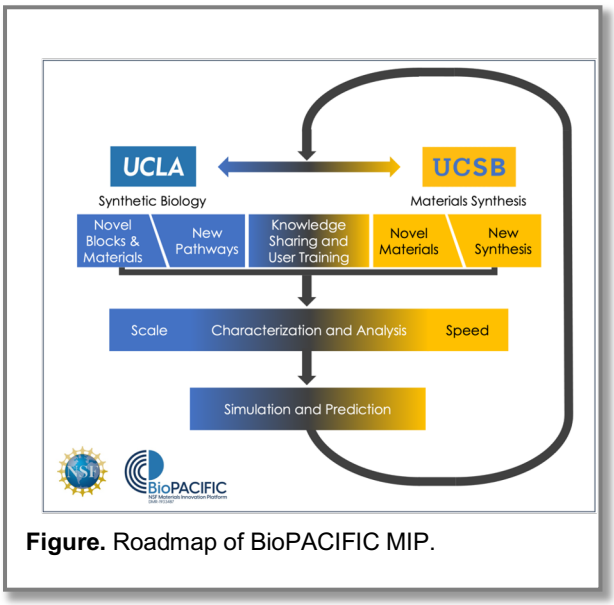


Figure. Roadmap of BioPACIFIC MIP.

Relevance to MGI
BioPACIFIC MIP's in-house research program is dedicated to advancing materials research using the MGI approach by integrating high-throughput experimental methods, cutting-edge characterization tools, and data science. To accomplish this goal, the program is structured around four fundamental research projects, called Synergistic Exploratory Thrusts (SETs).

SET 1: Bioderived Materials. SET 1 aims to harness natures exquisite biosynthetic machineries to produce valuable molecular entities, some of which are out of reach using traditional synthetic chemistry. The SET is focused on the discovery, engineering, and application of these machineries to produce natural products, monomers, and polymers with tunable properties.

SET 2: Sequence-defined Materials. SET 2 is a launch point for the development and understanding of sequence-defined polymers as novel functional soft materials. In its longevity, SET 2 endeavors to apply the relationships between monomer sequence and nanoscale structure to control macroscopic material properties at will, developing next-generation functional materials such as lithographic photoresists.

SET 3: Functional Biomimics. SET 3 focuses on creating guidelines for soft materials used in tissue-device applications, including biosensors, drug delivery systems, soft implants and stimuli-responsive materials. This work

strives to develop robust synthetic platforms using bio-derived building blocks and high-throughput methods to study the interactions between materials and living systems.

SET 4: Degradation-optimized Materials. SET 4 seeks to develop new bio-derived monomers and degradable polymers, coupled with novel strategies for facilitating and monitoring degradation. Emphasis is placed on high-throughput methods and analyses to characterize polymer degradation in different environments, from dilute solutions to bulk samples subjected to a range of conditions.

Development Projects: The in-house research program also aims to enhance the impact of the BioPACIFIC MIP facility by improving tool capabilities and refining standard operational procedures for MIP tools and users. This is achieved through development projects conducted by in-house researchers and project scientists. When in-house SETs or development projects establish a workflow on MIP tools, the process can be replicated with significantly less effort. These pre-existing methods serve as templates to construct a distinct workflow on the MIP tools, which are then made available to users.

Technical Progress

Technical developments in research, the user program, workforce development and knowledge sharing are available to the broad community via the BioPACIFIC MIP website (https://biopacificmip.org/).

Future Plans

BioPACIFIC MIP is focused on leveraging the entire MIP facility and integrating the MGI approach to accelerate research discoveries in bio-based materials.

Broader Impacts and Workforce Development

BioPACIFIC MIP focuses on building a strong and collaborative community through various knowledge-sharing and workforce development activities, including sharing tools, codes, samples, data, and know-how with both the in-house and user communities.

Data Management and Knowledge Sharing

The BioPACIFIC MIP shared experimental facilities serve as an interdisciplinary research nexus that promotes a culture of knowledge sharing through collaboration and scientific discourse. These facilities are deliberately managed and staffed with technical experts that impart knowledge by training researchers on the proper setup and use of equipment to properly carry out and analyze experiments, and moreover, expand and retain the MIP's institutional knowledge base through hands-on interaction with the users.

This research infrastructure provides the foundational framework to sustain and strengthen the future impact of the BioPACIFIC MIP, with the scientific community benefiting from shared knowledge, methods, and materials. Sharing is not a one-way flow of information out of the MIP but rather a collaborative partnership between BioPACIFIC MIP and its users. Users bring new knowledge to the MIP while also learning from it. This knowledge sharing is tightly integrated with the development of the Biosynthetic Pathways and Monomer Libraries and with a comprehensive Laboratory Information Management System (LIMS). BioPACIFIC MIP's LIMS system was created from the ground up as a mechanism to streamline the collection of instrument data across the center into a single data repository.

Advancing Along the Materials Development Continuum and Partnerships to Translation

BioPACIFIC MIP's mission is to integrate high-throughput synthetic biology and synthetic chemistry methodologies to develop advanced bioderived materials. This is accomplished through the operation of a national user facility for sustainable materials research that integrate cutting-edge, lab of the future research infrastructure and collaborative expertise to catalyze innovation and foster the sharing of knowledge and data.

Publications and References

1. M. Le, I. Lapkriengkri, K. Albanese, P. Nguyen, C. Tran, J. Blankenship, R. Segalman, C. Bates, M. Chabinyc, "Engineering Soft, Elastic, and Conductive Polymers for Stretchable Electronics Using Ionic Compatibilization". *Chem. Mater.* **35**, 7301–7310 (2023). https://doi.org/10.1021/acs.chemmater.3c01685.
2. K. Albanese, J. Blankenship, T. Quah, A. Zhang, K. Delaney, G. Fredrickson, C. M. Bates, C. J. Hawker "Improved Elastic Recovery from ABC Triblock Terpolymers". ACS Polym. Au. **5**, 376–382 (2023). https://doi.org/10.1021/acspolymersau.3c00012.
3. Y. Luo, M. Gu, M. Park, X. Fang, Y. Kwon, J. M. Urueña, J. Read de Alaniz, M. Helgeson, C. Marchetti, M. Valentine "Molecular-scale substrate anisotropy, crowding and division drive collective behaviours in cell monolayers" *J. R. Soc. Interface,* **20**, 20230160 (2023). https://doi.org/10.1098/rsif.2023.0160.
4. K. R. Albanese, Y. Okayama, P. T. Morris, M. Gerst, R. Gupta, J. C. Speros, C. J. Hawker, C. Choi, J. Read de Alaniz, and C. M. Bates "Building Tunable Degradation into High-Performance Poly(acrylate) Pressure-Sensitive Adhesives". *ACS Macro Lett.* **12**, 787−793 (2023). https://doi.org/10.1021/acsmacrolett.3c00204.
5. R. V. Garcia, E. A. Murphy, N. J. Sinha, Y. Okayama, J. M. Urueña, M. E. Helgeson, C. M. Bates, C. J. Hawker, R. D. Murphy, J. Read de Alaniz. "Tailoring Writability and Performance of Star Block Copolypeptides Hydrogels through Side-Chain Design". *Small,* **19**, 2302794 (2023). https://doi.org/10.1002/smll.202302794.
6. S. J. Bailey, E. Hopkins, N. Baxter, I. Whitehead, J. Read de Alaniz, M. Z. Wilson. "Diels-Alder Photoclick Patterning of Extracellular Matrix for Spatially Controlled Cell Behaviors". *Adv. Mater.* **35**, 2303453 (2023). https://doi.org/10.1002/adma.202303453.
7. M. Gu, X. Fang, Luo. "Data-Driven Model Construction for Anisotropic Dynamics of Active Matter". *PRX LIFE 1*, 013009 (2023). https://doi.org/10.1103/PRXLife.1.013009
8. H. P. Truong, S. Mengel, B. Yu, R. A. Segalman, O. A. Saleh**.** "Single-Molecule Polypeptoid Stretching Reveals the Effects of Charge Sequence on Chain Conformation". *Macromolecules,* **56**, 8558–8564 (2023). https://doi.org/10.1021/acs.macromol.3c01221
9. M. Nguyen, K. Dolph, K. T. Delaney, K. Shen, N. Sherck, S. Kohler, R. Gupta, M. B. Francis, M. S. Shell, G. H. Fredrickson. "Molecularly informed field theory for estimating critical micelle concentrations of intrinsically disordered protein surfactants". *J. Chem. Phys.* **159**, 244904 (2023). https://doi.org/10.1063/5.0178910.
10. N. J. Sinha, K. C. Cunha, R. Murphy, C. J. Hawker, J.-E. Shea, M. E. Helgeson. "Competition between β-Sheet and Coacervate Domains Yields Diverse Morphologies in Mixtures of Oppositely Charged Homochiral Polypeptides". *Biomacromolecules,* **24**, 3580–3588 (2023). https://doi.org/10.1021/acs.biomac.3c00361.
11. C. Ambra, M. Czuczola, P. Getty, E. Murphy, A. Abdilla, S. Biswas, J. Mecca, T. Bekemeier, S. Swier, C. M. Hawker, C. M. Bates. "Versatile synthesis of siloxane-based graft copolymers with tunable grafting density". *J Polym Sci.* **62**, 92–101 (2024). https://doi.org/10.1002/pol.20230615.
12. A. DeStefano, S. Mengel, M. Bates, S. Jiao, S. Shell, S. Han, R. Segalman. "Control over Conformational Landscapes of Polypeptoids by Monomer Sequence Patterning". Macromolecules **57**, 1469–1477 (2024). https://doi.org/10.1021/acs.macromol.3c02338.
13. M. J. Dror, J. Misa, D. A. Yee, A. M. Chu, R. K. Yu, B. B. Chan, L. S. Aoyama, A. P. Chaparala, S. E. O'Connor, Y. Tang. "Engineered biosynthesis of plant heteroyohimbine and corynantheine alkaloids in Saccharomyces cerevisiae". *J. Ind. Microb. Biotechnol.* **51**, kuad047 (2024**)**. https://doi.org/10.1093/jimb/kuad047.
14. D. J. Atkins, J. M. Rosas, L. K. Månsson, N. Shahverdi, S. S. Dey, A. A. Pitenis. "Survival-Associated Cellular Response Maintained in Pancreatic Ductal Adenocarcinoma (PDAC) Switched Between Soft and Stiff 3D Microgel Culture". *ACS Biomater. Sci. Eng.* **10**, 2177–2187 (2024). https://doi.org/10.1021/acsbiomaterials.3c01079
15. T. Göckler, F. Albreiki, D. Li, A. Grimm, F. Mecklenburg, J. M. Urueña, U. Schepers, S. Srivastava. "Block Polyelectrolyte Additives That Modulate the Viscoelasticity and Enhance the Printability of Gelatin Inks at Physiological Temperatures". *ACS Appl. Polym. Mater.* **6**, 2427−2441 (2024). https://doi.org/10.1021/acsapm.3c01085
16. J. Chen, V. Bhat, C. J. Hawker. "High-Throughput Synthesis, Purification, and Application of Alkyne-Functionalized Discrete Oligomers". *J. Am. Chem. Soc.* **146**, 8650–8658 (2024). https://doi.org/10.1021/jacs.4c00751
17. K.-C. Yang, D. Mirabal, R. Garcia, N. Vlahakis, P. Nguyen, S. Mengel, M. Mecklenburg, J. Rodriguez, S. Shell, C. J. Hawker, R. Segalman. "Crystallization-Induced Flower-like Superstructures via Peptoid Helix Assembly". *ACS Macro Lett.* **13**, 423–428 (2024). https://doi.org/10.1021/acsmacrolett.4c00039 .

Accelerating the Commercial Readiness of Organic Semiconductor Systems (ACROSS)

Lead Investigator: Chad Risko, chad.risko@uky.edu
Participating Institutions: University of Kentucky (UK), Wake Forest University (WFU), Princeton University (PU)
Source of Support: NSF-DMREF Award Nos. 2323422, 2323423, 2323424
Website: https://oscar.as.uky.edu/
Keywords: organic semiconductors; processing–structure co-design; thin-film transistors; radiation dosimeters

Project Scope

The multi-scale and multi-parameter natures of electronic and optical processes in organic semiconductors (OS) are critical features that determine materials function. These characteristics, coupled with the need for material uniformity over large areas and environmental and operational stability, currently inhibit the widespread adoption of OS in commercial applications. ACROSS is developing data structures and machine learning (ML) models that bring together insights from theory, materials synthesis and characterization, and device development and operation with the goal to produce OS for applications that span prototype thin-film transistors (TFT) and radiation dosimeters to TFT arrays and radiation imagers.

Relevance to MGI

The ACROSS mission is to determine the factors and derive the associated data structures and tools for machine-informed discovery of molecular OS with prescribed properties, yielding operationally stable electronic devices with uniformity over application-relevant device areas. ACROSS has as its cornerstone a team with more than a decade of collaboration of over a decade that has established highly integrated feedback loops between materials synthesis and characterization, modeling, data infrastructure development, ML, and device testing and implementation efforts across three universities. An example of our team's success is OCELOT (Organic Crystals for Electronic and Light Oriented Technologies; NSF DMREF Award Nos. 1627428, 1627453, 1627925), a publicly accessible data infrastructure to deposit and access experimental and computational data for π-conjugated molecules and OS that is further enhanced with easy to access and use ML models to predict molecular electronic, redox, and optical properties and OS charge-carrier transport properties. ACROSS will build on this success by: Expanding OCELOT and increasing access for the user community; developing and integrating software to capture OS characterization and device data into structured formats to enable ML models geared towards prescribed property prediction and optimization; synthesizing ML-guided OS optimized for high charge-carrier mobilities, radiation sensitivity, and operational stability; and prototyping ML-guided OS deposition and processing conditions for prototype TFT and radiation dosimeters and larger-area TFT arrays and radiation imagers.

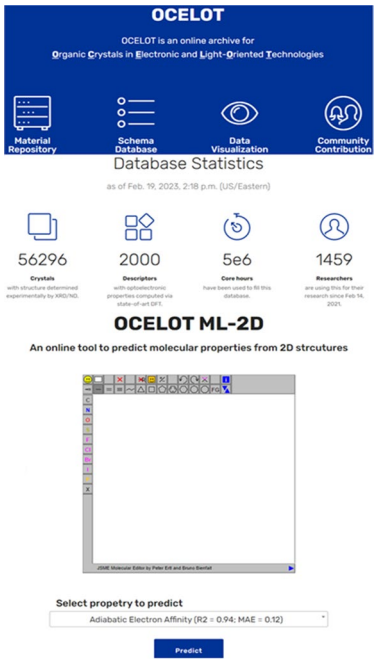


Figure. OCELOT provides experimental and computational data and access to ML models for property prediction.

Technical Progress

Efforts over the first year of ACROSS have focused on three key areas. While our initial ML developments focused on predicting properties of molecules or OS for which structures are known, we have turned our focus to developing ML models that allow us to predict new molecular structures that could be of interest as OS building blocks and packing configurations in the solid state. These developments include the use of active learning approaches to both expedite model training and allow for model training on small data sets. As an example of workflow, ACROSS has also developed a new OS building block that aims to limit the impact of low-energy phonon modes in OS. These so-

called “killer” phonon modes impact the intermolecular electronic couplings, critical descriptors for OS charge-carrier transport. These OS are now being tested in TFT, and the processing parameters are being refined to ensure reliable and large-area processing.

Future Plans

OS present tremendous potential, though several challenges remain to realize widespread commercialization. ACROSS bridges the elucidation of fundamental chemical, materials, and physical insights with the development of data-informed, machine-based discovery models to enable the practical production of large-area and stable OS-based devices through solution or melt processing. With a focus on TFT arrays and radiation sensing as application testbeds, ACROSS will leverage and expand on the achievements of our highly multidisciplinary team to create knowledge and tools for the global OS community that, given the problems to be addressed, will expand beyond the discipline. The ACROSS research objectives are to: 1) Expand machine-informed OS-design tools and access through extension of an already-comprehensive data infrastructure and associated machine-learning (ML) infrastructure; 2) co-design molecular and crystal/material structures and processing parameters to facilitate the development of OS that are spreadable over large areas with uniform and stable prescribed properties; and, 3) apply optimized OS and process conditions to create uniform, high-performance, stable TFT arrays and X-ray detectors across large areas. Through these objectives, ACROSS will demonstrate how the convergence of materials synthesis and characterization, theory, data science and ML, and device implementation can enable stable OS that can be fabricated over large areas and maintain prescribed and uniform metrics in different application testbeds.

Broader Impacts and Workforce Development

The ACROSS research and infrastructure sets the foundation for our broader impacts. The ACROSS team has a strong track record of collaborative publication, invited presentations, and conference organization. Key milestones will be available on the ACROSS website. ACROSS seeks to develop a diverse MGI-ready workforce knowledgeable in experimentation, computation, data infrastructures, and device implementation. Three ACROSS PIs work in regions adjacent to Appalachia, a region whose inhabitants are significantly underrepresented in the scientific community. We are collaborating with academic colleagues in these rural regions (e.g., eastern KY, western NC) to bring undergraduates into the ACROSS team and prepare them for employment in today’s highly technical and collaborative workplace. Risko and Anthony (UK) have also worked with faculty in these regions to assist them in preparing and submitting proposals to federal funding agencies. Undergraduate Edy Mackenzie (WFU; Jurchescu) is participating in a summer internship at PU with Loo. ACROSS PIs participate in meetings and tours with Federal and State officials, members of local industries, and K-12 students and teachers. All PIs have modules for K-12 audiences, and ACROSS PIs are members of consortia to include high school students in research.

Data Management and Open Access

The OCELOT (https://oscar.as.uky.edu/) web-user interface (WUI) and Python-based application programming interface (API) interact with OCELOT, a MongoDB database. OCELOT is FAIR compliant. Snapshots of OCELOT and raw computational data are regularly backed-up on network-attached storage. The WUI provides interactive and programmatic access to the database, where the schema are documented for data interoperability; data can be downloaded in several formats. Copies of OCELOT data are available through the NIST MDF. Select OSCAR experimental data are provided on OCELOT. All OSCAR papers provide data both in the manuscript and supporting information (SI), and example input computational files are provided in SI and on OCELOT.

Advancing Along the Materials Development Continuum and Partnerships to Translation

ACROSS seeks to accelerate OS commercialization by combining necessary advances in fundamental chemical, materials, and physical insights with the development and implementation of data-informed, machine-based discovery models that bridge molecular design and materials processing to enable the production of large-area and stable OS-based devices. The combined expertise of the ACROSS team is distinct in the field, and the team has already moved the limits of what can be achieved through our efforts. The ACROSS team is also highly collaborative, counting numerous academic and national laboratory collaborators. ACROSS will continue to expand our reach through collaborations with several partners in NIST, whose focus is on commercialization, and through efforts to identify entrepreneurship opportunities and new industrial partnerships. The ACROSS team has also made all of our data and data infrastructures, software, and ML models open access. We foresee opportunities to use our insights in other fields, broadening the reach the ACROSS vision.

Publications and References

1. P. Sundaram, R.B. Spencer, A. Tiwari, S.J. Whittaker, T. Mandal, Y. Yang, E.K. Holland, C.J. Kingsbury, M. Klopfenstein, J.E. Anthony, B. Kahr, S. Jeong, A.G. Shtukenberg, and S.S. Lee. *Polymer-Assisted Polymorph Transition in Melt-Processed Molecular Semiconductor Crystals*, Chemistry of Materials, Early Access (2024). DOI10.1021/acs.chemmater.4c00418.
2. F. Maleki, K.J. Thorley, H.F. Iqbal, D. Vong, T. Maitra, A. Petty, L.L. Daemen, S.R. Parkin, O.D. Jurchescu, J.E. Anthony, and A.J. Moulé, *Design Rules to Optimize the Intermolecular and Long-Range Packing of Organic Semiconductor Crystals,* Chemistry of Materials, 36, Chemistry of Materials, 36, 9, 4794-4805 (2024). DOI: 10.1021/acs.chemmater.4c00640.

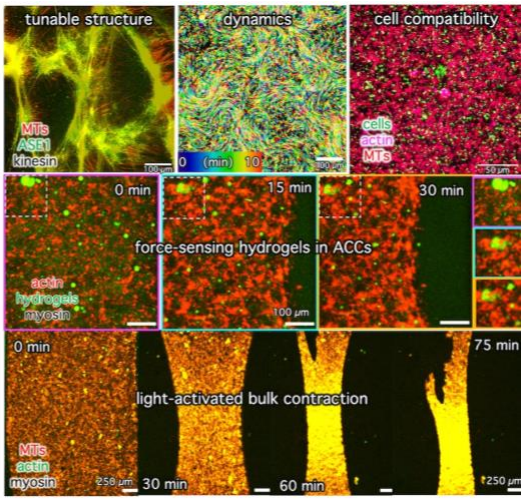
Collaborative Research: DMREF: Living biotic-abiotic materials with temporally programmable actuation

Lead Investigator: Rae Robertson-Anderson, randerson@sandiego.edu
Participating Institutions: University of San Diego (R.M. Robertson-Anderson, R. McGorty), Rochester Institute of Technology (M. Das), Syracuse University (J.L. Ross), University of Chicago (M. Rust), University of California – Santa Barbara (M.T. Valentine, M.Gu)
Website: www.livingbam.org
Keywords: Active Matter, Synthetic Biology, Biomaterials, Cytoskeleton, Programmable, Soft Matter

Project Scope: We will develop foundational technologies, predictive models, and formulation libraries to pioneer a new class of autonomous reconfigurable materials with self-generated spatiotemporal control. Guided by multi-scale modeling, and leveraging advances in synthetic biology and active matter, we will integrate biological circuits into biotic-abiotic composites to engineer materials that self-actuate programmable work cycles. Our design paradigm couples hydrogels to living cytoskeleton layers infused with bacteria that secrete cytoskeleton-modifying proteins on a programmable schedule. Our proof-of-concept design target will be a gap-closing micro-actuator that photo-responsively closes and autonomously re-opens at times and locations programmed into the cells.

Relevance to MGI: We will capitalize on our team's unique expertise and strong collaborative track record to engineer living biotic-abiotic materials (BAMs) that unite microbes, proteins, biopolymers, and hydrogels, for in situ bioproduction and self-regulation to autonomously drive actuation and perform work. Our proof-of-concept photo-responsive devices and materials will serve as a powerful testbed that can be leveraged by us and the broader MGI community to manufacture and deploy autonomous BAMs. We will use iterative design, build, test, learn (DBTL) cycles to accelerate discovery–linking theory, fabrication, computation, and characterization to establish a broad phase space of structure-mechanics-function relationships. We will partner with NSF BioPACIFIC Material Innovation Platform (MIP, DMR-1933487) to develop high-throughput screening schema and formulation libraries to rapidly optimize and publicly share our material blueprints and technologies. Our strong team and dissemination plans, along with robust training opportunities for the next generation of MGI researchers–from high school students to postdocs–will empower the MGI community to leverage our discoveries to engineer programmable dynamic devices and materials.

Technical Progress: Progress under each Aim is described below.
Aim 1. Curate and disseminate a comprehensive platform to design, build, test, and learn from active biotic-abiotic material (BAM) actuators optimized for stiffness, strength, and contractility. We have focused much of our efforts on developing the tools and workflows for screening, characterization, and dissemination of active, soft and biological materials for the broader MGI community. We are developing high-throughput screening software that can 'fingerprint' complex dynamic materials by key features of their dynamics and structure. The development of this software, BARCODE (Biomaterial Activity Readouts to Categorize, Optimize, Design and Engineer) has been accelerated through two hackathons with 5 faculty and 20 trainees (2 high school students, 8 graduate students, 4 undergraduates, 2 postbacs, 4 postdocs) funded by our 2022 DMREF supplement. We are also developing a searchable database SMARTBANK (Soft, Multicomponent, Active, Resilient, Tough, Biomaterials to Advance New Knowledge) to share materials compositions and properties of soft, biological and active materials. The development and deployment of this database was driven by 2 high school students working cooperatively within our team, and we are now testing it internally to share data across campuses and with BioPACIFIC staff to optimize the design before launch. We continue to develop in vitro and in silico Active Cytoskeletal Composites



BAM prototypes demonstrating performance targets. (Top) ACCs can be tuned to have strong cable-like structure (left), active dynamics (middle), and compatibility with cells (right) needed for Aim 3. (Middle) deformation of hydrogels (green) in contracting ACCs can read-out force. Right images are zoom-ins of the boxed regions in each image in the time-series. (Bottom) Bulk contraction and rupture of light-activated ACC.

(ACCs) including: optimizing protocols for reproducibility, extending lengthscales of contractile dynamics, introducing light-activation of myosin and kinesin motors, expanding the toolkit of binding proteins to optimize performance, and improving hydrogel sensing and coupling capabilities. We presented these results at APS March Meetings (2023, 2024) and 2023 Biophysical Society (BPS) Meeting.

Aim 2. Develop cyanobacteria as a programmable synthetic biology platform able to deliver molecules according to a user-defined schedule. We have engineered cyanobacteria to include the gene that expresses thymosin, a protein which depolymerizes actin upon secretion and should be small enough to allow for efficient secretion. We have developed assays and experiments to determine required concentrations of depolymerizing cofactors and time scales for actin network depolymerization. We presented these results at the 2023 APS March and BPS Meetings.

Aim 3. Integrate biotic-abiotic actuators and living bioproduction elements to create programmable autonomous materials. We have assessed the properties of ACCs in the presence of varying concentrations of cells to determine the extent to which ACCs maintain their robust properties, and the impact cells have on the structure and dynamics. We have determined that for a wide range of ACC compositions, cells remain uniformly dispersed throughout the ACCs which themselves remain connected with minimal structural alteration. We presented these results at the 2024 APS March Meeting, and are currently developing in-silico models informed by these experiments.

Future Plans

1. We will curate and disseminate a comprehensive DBTL platform of active BAM actuators optimized for stiffness, strength, and contractility. We will optimize and disseminate BARCODE and SMARTBANK as powerful tools for the MGI community. We will build on BARCODE to develop advanced data-driven analysis algorithms, informed by predictive modeling that we will be optimizing in the coming months. We will continue to build the formulation-mechanics library of our ACCs and work towards optimal coupling to abiotic hydrogels. We will test and iteratively optimize predictions from multi-scale mechanistic models and new active matter theories.

2. We will develop cyanobacteria as a programmable synthetic biology platform to deliver molecules within materials according to a user-defined schedule. We will pioneer foundational advances in the synthetic biology of cyanobacteria to enable living cells to generate programmable waves of gene expression and secretion of cytoskeleton-modifying proteins, driven by their circadian clock, to empower living biotic-abiotic materials.

3. We will integrate biotic-abiotic actuators and living bioproduction elements to create programmable autonomous materials. Employing the design strategies and tools developed in Aims 1 and 2, we will engineer materials that can execute designed yet autonomous actions on a programmable schedule through in situ production of material-modifying proteins. We will incorporate bacteria with genetically-encoded timing circuits into BAM actuators (to program ACC disassembly via timed secretion of the depolymerization factors (e.g., thymosin), providing a programmable off-switch to BAM actuators. Through iterative DBTL cycles, and leveraging multiple engineered cells with different oscillator frequencies, we will construct complex temporal programs of self-actuated material restructuring and force-generation, and decode and encode design rules for programmable living materials.

Broader Impacts and Workforce Development: We engaged a diverse team of high school students, undergraduates, postbacs, graduate students, and postdocs, broadening participation of URM, women and first-generation researchers, and providing rich professional development opportunities including presenting at virtual and in-person project meetings and national conferences. Trainees across campuses collaborate through our project slack channel, trainee-led sidebar meetings, collaborative projects, and in-person workshops and hackathons to arm students with skills to lead a world-class materials workforce. We have also developed a strong track record of co-mentoring trainees to provide experiences in true team approaches to discovery and professional networking.

Data Management and Open Access: BARCODE and SMARTBANK are both in testing phases, to be optimized and launched publicly within the year. Characterization code is available via GitHub and results disseminated via conference presentations, publications and PI websites and www.livingbam.org.

Advancing Along the Materials Development Continuum and Partnerships to Translation: Our materials platform will result in novel technologies and predictive design paradigms for temporally-encoded autonomous materials with applications in self-propulsive and self-sensing materials, programmable prosthetics, micro-robotics, adaptive optics, and self-healing infrastructure. The synthetic biology tools, models, HTP screening software, and materials database we develop will transform future studies of active soft materials, enable use of engineered cyanobacteria for material modulation, and provide critical inputs to ML algorithms for material design. We continue to partner with local industry and foundation sponsors to host annual symposia (www.sdsoftmatter.com) where we share our results with the academic and industrial active matter and synthetic biology communities.

Publications

1. RM Robertson-Anderson. optical tweezers microrheology maps micro-mechanics of complex systems. *Trends in Biochemical Sciences* (2024). doi:10.1016/j.tibs.2024.04.009.
2. RM Robertson-Anderson. Molecular motors make waves and sculpt patterns. *Nature Physics* (2024). doi:10.1038/s41567-023-02286-y
3. RJ McGorty, CJ Currie, J Michel, M Sasanpour, C Gunter, KA Lindsay, MJ Rust, P Katira, M Das, JL Ross, RM Robertson-Anderson. Kinesin and myosin motors compete to drive rich multiphase dynamics in programmable cytoskeletal composites. *PNAS nexus*, 2, pgad245 (2023). doi: https://doi.org/10.1093/pnasnexus/pgad245
4. N. Krishnan, N. Sarpangala, M. Gamez, A. Gopinathan, J.L Ross, Effects of Cytoskeletal Network Mesh Size on Cargo Transport. *European Physical Journal E.* 46, 109 (2023) doi: 10.1140/epje/s10189-023-00358-8
5. M Sasanpour, DH Achiriloaie, G Lee, G Leech, C Currie, KA Lindsay, JL Ross, RJ McGorty, RM Robertson-Anderson. Reconstituting and characterizing actin-microtubule composites with tunable motor-driven dynamics and mechanics. *JoVE (Journal of Visualized Experiments)*, 186, e64228 (2022). doi: 10.3791/64228
6. J. Michel, G. von Kessel, T. Wyse Jackson, L. Bonassar, I. Cohen, and M. Das, Reentrant rigidity percolation in structurally correlated filamentous networks, Phys. Rev. Research 4, 043152 (2022). doi:10.1103/PhysRevResearch.4.043152
7. HN Verwei, G Lee, G Leech, II Petitjean, GH Koenderink, RM Robertson-Anderson, R McGorty. Quantifying Cytoskeleton Dynamics Using Differential Dynamic Microscopy. *JoVE*, 184, e63931 (2022). doi: 10.3791/63931

Uncovering Mechanisms of Grain Boundary Migration in Polycrystals for Predictive Simulations of Grain Growth

Lead Investigator: Gregory S. Rohrer, gr20@andrew.cmu.edu
Participating Institutions: Carnegie Mellon University, The University of Michigan
Source of Support: NSF-DMREF
Website: none
Keywords: Grain growth, Grain boundaries, Polycrystals, Microstructure

Project Scope

Grain boundary network structures are determined by grain boundary migration when the material is processed at high temperature. Therefore, controlling materials properties is predicated on understanding and controlling grain boundary migration. X-ray microscopy has been used to measure microstructure evolution in ferritic iron, nickel, and strontium titanate. The results are compared to mesoscale and atomistic simulations of grain boundary migration to refine existing models. Understanding the mechanism of interface migration will make it possible to better predict microstructure evolution, a necessary step in accelerating the development of polycrystalline materials.

Relevance to MGI

It has been common practice for designers to incorporate metallic and ceramic components into structures and devices assuming uniform and fixed bulk properties. However, a material's properties are sensitive to the types of interfaces within the material and this is a result of materials processing. To make materials part of the design process, it is necessary not only to know the range properties available, but also how to achieve them though processing. This project's aim of developing accurate predictive simulations for microstructure evolution will accelerate the incorporation of polycrystalline components by defining processing conditions to achieve specific microstructures and properties. This is integral to the broader goals of the Materials Genome Initiative.

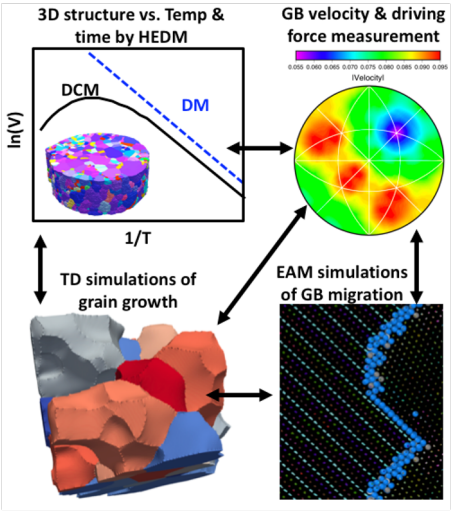


Figure. Illustration of the project activities and how they are related. We have measured grain boundary velocities and their correlations with grain boundary properties. The same data are used to instantiate atomistic and continuum simulations will be used to interpret the observed microstructure evolution.

Technical Progress

We have combined experimental measurements with continuum and atomistic models to study grain boundary migration and grain growth. Both simulations use experimental data as input so that a direct comparison can be made to the experiment.

The continuum simulation uses a threshold dynamics model of grain growth that accounts for the anisotropy in the grain boundary energy. The simulation reproduces several aspects of the observed microstructural evolution that are not found in the results of simulations assuming isotropic properties. For example, the relative areas of the lowest energy twin boundaries increase as the grains grow and the average grain boundary energy decreases with grain growth. This decrease in energy occurs because the population of higher energy grain boundaries decreases while the population of lower energy boundaries increases as the total grain boundary area decreases. This phenomenon emerges from the assumption of anisotropic grain boundary energies without modification of the energy minimizing algorithm. These findings are consistent with the experimental observation that in addition to

the decrease in grain boundary area, additional energy is dissipated during grain growth by a decrease in the average grain boundary energy.

Molecular dynamics simulations of grain growth in polycrystalline nickel were executed to investigate the relationship between grain boundary curvature and velocity. A bidirectional method for converting data between voxelized and atomic structures was developed and validated. The outcomes of the MD grain growth simulation broadly matches the characteristics of grain growth observed in the experiment. Most significantly, the simulation result contributes additional evidence supporting the reported absence of a correlation between velocity and curvature during grain growth in polycrystals, and confirms that this is not related to solutes, precipitates, processing route, or characterization method. The implication is that features of the 3D grain boundary network interfere with the velocity/curvature relationship.

The main findings from our combined experiments and simulations follow. First, based on experiments conducted on $SrTiO_3$, α-Fe, and Ni, the grain boundary curvature has been shown to be a poor predictor of the direction and speed of migration of grain boundaries in polycrystals, demonstrating a significant deficiency in the conventional theory. This experimental finding is substantiated by the simulations. Second, polycrystalline microstructures dissipate energy by changing the types of boundaries in the population, accumulating low energy boundaries and annihilating higher energy boundaries. This provides an additional driving force for grain boundary migration that is ignored in the conventional theory. Third, most aspects of this new migration phenomenon can be reproduced only if the simulations account for the anisotropy of the grain boundary energy. This indicates the important role that grain boundary energy anisotropy plays in determining the driving force for migration.

Future Plans

While we now have ample evidence that there is a driving force for migration that is related to the grain boundary energy anisotropy, we do not have an analytic expression for this. Our current and future work is to develop a model and analytic expression to predict grain boundary migration. We are currently analyzing the experimental and simulation data to find coarse grained descriptors to correlate the motion of grain boundaries with their energies.

Broader Impacts and Workforce Development

We annually hold a workshop on 3D microstructure studies. The workshop consists of three types of presentations. Roughly one third of the presentations are about state of the art 3D materials research. Another third are tutorials illustrating the capabilities and uses of Dream.3D. The final third of the workshop consists of practical sessions in which participants work on individual projects with the guidance of the speakers. Each year, about 50 participants from industry, government labs, and universities learn about 3D microstructure characterization tools developed and used as part of this project. See: http://mimp.materials.cmu.edu/rohrer/3DMS_workshop_24/

Data Management and Open Access

The experimental data, analysis code, and simulation code used in this project are available in internet repositories, listed below:
Data: http://mimp.materials.cmu.edu/~gr20/Grain_Boundary_Data_Archive/
Analysis code: https://github.com/gr20cmu/gbXstallography
Examples of using analysis code and data: http://mimp.materials.cmu.edu/rohrer/gbXstallography/
Grain boundary energy reconstruction code: https://github.com/Yufeng-shen/TJ2GBE
Simulation code: https://github.com/JadeXiaoyaoPeng/GrainGrowth_TD_iso
Simulation code: https://github.com/Kiana-Naghibzadeh/TD_aniso_BRK

Advancing Along the Materials Development Continuum and Partnerships to Translation

We have collaborated with NIST on developing accelerated EBSD data collection strategies and Xnovotech and the interpretation of 3D X-ray microscopy data. These projects are ongoing.

Publications and References[1-16]

All peer-reviewed publications associated with this project are listed on the next page.

Peer-reviewed publications associated with this project

[1]R. Cavuoto, A. Cutolo, K. Dayal, L. Deseri, and M. Fraldi, "Distal and non-symmetrical crack nucleation in delamination of plates via dimensionally-reduced peridynamics," *J. Mech. Phys. Sol.,* **172** (2023). https://doi.org/10.1016/j.jmps.2022.105189
[2]J. Chua, V. Agrawal, T. Breitzman, G. Gazonas, and K. Dayal, "Phase-field modeling and peridynamics for defect dynamics, and an augmented phase-field model with viscous stresses," *J. Mech. Phys. Sol.,* **159** (2022). https://doi.org/10.1016/j.jmps.2021.104716
[3]S. Florez, K. Alvarado, B. Murgas, N. Bozzolo, D. Chatain, C. E. Krill, M. Y. Wang, G. S. Rohrer, and M. Bernacki, "Statistical behaviour of interfaces subjected to curvature flow and torque effects applied to microstructural evolutions," *Acta Mater.,* **222** 117459 (2022). https://doi.org/10.1016/j.actamat.2021.117459
[4]M. Hakimzadeh, V. Agrawal, K. Dayal, and C. Mora-Corral, "Phase-field finite deformation fracture with an effective energy for regularized crack face contact," *J. Mech. Phys. Sol.,* **167** 104994 (2022). https://doi.org/https://doi.org/10.1016/j.jmps.2022.104994
[5]C. E. Krill, E. A. Holm, J. M. Dake, R. Cohn, K. Holíková, and F. Andorfer, "Extreme Abnormal Grain Growth: Connecting Mechanisms to Microstructural Outcomes," *Ann. Rev. Mater. Res.,* **53** 319-45 (2023). https://doi.org/10.1146/annurev-matsci-080921-091647
[6]M. Lyu, Z. Xu, G. S. Rohrer, and E. A. Holm, "Comparing Molecular Dynamics Simulations of Grain Growth with Experimental Data," *Scripta Mater.,* **Submitted** (2024). https://doi.org/http://dx.doi.org/10.2139/ssrn.4827552
[7]J. A. Mitchell, F. Abdeljawad, C. Battaile, C. Garcia-Cardona, E. A. Holm, E. R. Homer, J. Madison, T. M. Rodgers, A. P. Thompson, V. Tikare, E. Webb, and S. J. Plimpton, "Parallel simulation via SPPARKS of on-lattice kinetic and Metropolis Monte Carlo models for materials processing," *Modelling Simul. Mater. Sci. Eng.,* **31** [5] (2023). https://doi.org/10.1088/1361-651X/accc4b
[8]V. Muralikrishnan, H. Liu, L. Yang, B. Conry, C. J. Marvel, M. P. Harmer, G. S. Rohrer, M. R. Tonks, R. M. Suter, C. E. Krill III, and A. R. Krause, "Observations of Unexpected Grain Boundary Migration in SrTiO3," *Scripta Mater.,* **222** 115055 (2023). https://doi.org/10.1016/j.scriptamat.2022.115055
[9]S. K. Naghibzadeh, N. Walkington, and K. Dayal, "Accretion and ablation in deformable solids with an Eulerian description: examples using the method of characteristics," *Math. Mech. Sol.,* **27** [6] 989-1010 (2022). https://doi.org/10.1177/10812865211054573
[10]S. K. Naghibzadeh, Z. Xu, D. Kinderlehrer, R. M. Suter, K. Dayal, and G. S. Rohrer, "Impact of Grain Boundary Energy Anisotropy on Grain Growth," *Phys. Rev. Mater.,* **Submitted** (2024).
[11]M. J. Patrick, G. S. Rohrer, O. Chirayutthanasak, S. Ratanaphan, E. R. Homer, G. L. W. Hart, Y. Epshteyn, and K. Barmak, "Relative grain boundary energies from triple junction geometry: Limitations to assuming the Herring condition in nanocrystalline thin films," *Acta Mater.,* **242** (2023). https://doi.org/10.1016/j.actamat.2022.118476
[12]X. Peng, A. Bhattacharya, S. K. Naghibzadeh, D. Kinderlehrer, R. Suter, K. K. Dayal, and G. S. Rohrer, "Comparison of simulated and measured grain volume changes during grain growth," *Phys. Rev. Mater.,* **6** (2022). https://doi.org/10.1103/PhysRevMaterials.6.033402
[13]A. Q. Qiu, I. Chesser, and E. Holm, "On the variability of grain boundary mobility in the isoconfigurational ensemble," *Acta Mater.,* **257** (2023). https://doi.org/10.1016/j.actamat.2023.119075
[14]G. S. Rohrer, I. Chesser, A. R. Krause, S. K. Naghibzadeh, Z. P. Xu, K. Dayal, and E. A. Holm, "Grain Boundary Migration in Polycrystals," *Ann. Rev. Mater. Res.,* **53** 347-69 (2023). https://doi.org/10.1146/annurev-matsci-080921-091511
[15]Z. Xu, C. M. Hefferan, S. F. Li, J. Lind, R. M. Suter, F. Abdeljawad, and G. S. Rohrer, "Energy dissipation by grain boundary replacement during grain growth," *Scripta Mater.,* **230** 115405 (2023). https://doi.org/https://doi.org/10.1016/j.scriptamat.2023.115405
[16]Z. Xu, Y.-F. Shen, S. K. Naghibzadeh, X. Peng, V. Muralikrishnan, S. Maddali, D. Menasche, A. R. Krause, K. Dayal, R. M. Suter, and G. S. Rohrer, "Grain boundary migration in polycrystalline α-Fe," *Acta Materialia,* **264** 119541 (2024). https://doi.org/https://doi.org/10.1016/j.actamat.2023.119541

Data Driven Design of High Entropy Oxides: A Collaboration of Two NSF Materials Innovation Platforms

Materials Innovation Platform: GlycoMIP
MIP Director: Maren Roman, maren.roman@vt.edu
MIP Associate Director: Robert J. Woods, rwoods@ccrc.uga.edu
MGI PI Meeting Participant in 2024: Sanket A. Deshmukh, sanketad@vt.edu
Participating Institutions: Virginia Tech, University of Georgia, Brandeis University, Rensselaer Polytechnic Institute
Source of Support: NSF-DMR.
Website: https://glycomip.org
Keywords: glycomaterials; carbohydrates; data driven design; composite machine learning.

Project Scope: GlycoMIP is an NSF Materials Innovation Platform that accelerates the discovery and development of glycomaterials, broadly defined as materials that contain or consist of carbohydrates. GlycoMIP advances the goals of the Materials Genome Initiative (MGI) through several multidisciplinary efforts, integrating experimental, theory-based, and data driven approaches to advance manufacturing, process automation, molecular design, material discovery, and outcome prediction. This report highlights one of these efforts, a collaboration between GlycoMIP and the NSF Platform for the Accelerated Realization, Analysis, and Discovery of Interface Materials (PARADIM), testing the transferability of a data driven design method developed for glycomaterials design to high entropy alloys and oxides **(Figure 1)**. The successful effort demonstrates the broader impact of the method.

Relevance to MGI: GlycoMIP has established both physical and digital infrastructures to foster glycomaterials innovation. Specifically, GlycoMIP operates physical national user facilities at Virginia Tech and the University of Georgia, housing state-of-the-art equipment for the synthesis, characterization, and modeling of glycomaterials. Additionally, GlycoMIP has developed a digital hub, accessible at https://glycodata.org to facilitate data sharing, data science approaches, and provide access to online tools.

Efforts by the GlycoMIP team to harness the power of data and integrate experimental and computational approaches have resulted in a number of impactful methods and tools, including a closed-loop additive manufacturing method,[1] autonomous/high-throughput/robotically directed characterization methods,[2-4] a theory-guided deep learning-enhanced biosensing method,[5,6] methods for data driven molecular design[7] and discovery,[8] and a chemical reaction prediction tool employing composite machine learning,[9] to name a few.

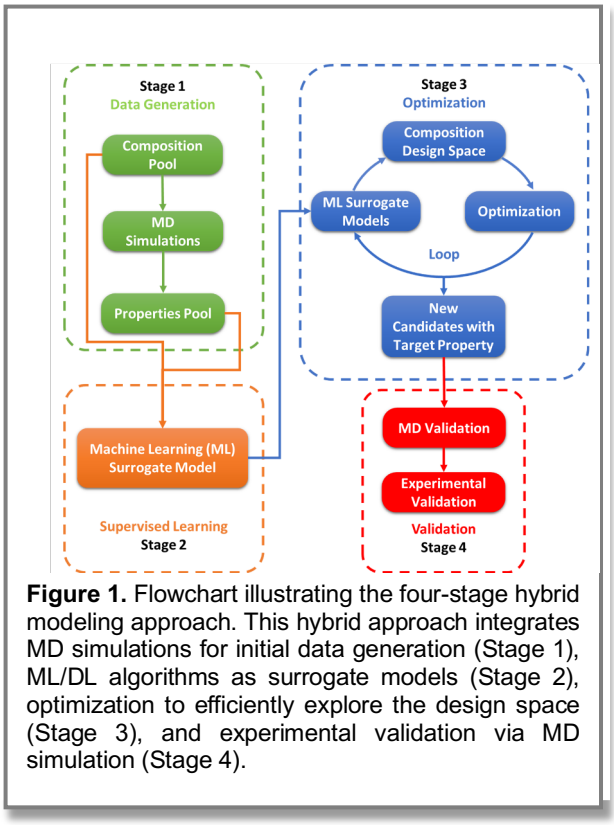


Figure 1. Flowchart illustrating the four-stage hybrid modeling approach. This hybrid approach integrates MD simulations for initial data generation (Stage 1), ML/DL algorithms as surrogate models (Stage 2), optimization to efficiently explore the design space (Stage 3), and experimental validation via MD simulation (Stage 4).

Technical Progress: The collaboration highlighted here, between Sanket Deshmukh (GlycoMIP, Virginia Tech) and Tyrel McQueen (PARADIM, Johns Hopkins University), tested the transferability of a data driven design method, developed by Deshmukh, to the design of high entropy oxides with desired properties. In the initial stage, the project focused on designing multi-principal component alloys (MPEAs). MPEAs composed of more than two principal elements and multiple non-principal elements offer enhanced corrosion resistance, mechanical properties, radiation resistance, and wear resistance. Given the vast design space offered by metal elements and their possible

compositions, using existing trial-and-error experimental methods to design an MPEA with desired properties is challenging. Using inverse design principles, the team designed FeNiCrCoCu MPEAs with superior mechanical properties compared to the equimolar MPEA with high unstacking fault energy (USFE, γusf), while understanding the role of individual elements and their chemical short-range order (CSRO) on these properties. Machine learning and deep learning models were trained using high-quality data from molecular dynamics (MD) simulations to predict USFE and bulk modulus of MPEAs **(Figure 1)**. These models were integrated with evolutionary algorithms to guide and accelerate the exploration of the design space for FeNiCrCoCu MPEAs. A selected composition of the newly designed MPEAs, when experimentally synthesized and tested, showed excellent agreement with computational predictions. The SHapley Additive exPlanations (SHAP) analysis of ML models revealed the relationships between the local arrangement of atoms in an alloy and its mechanical properties. This insight is useful for developing accurate predictive models for designing new MPEAs with desired properties. The data design framework is currently being optimized for the design of new high-entropy oxides.

Future Plans: Current, highly successful efforts to leverage data science approaches to accelerate glycomaterials discovery and development will be continued, while efforts to advance theory-based simulation and prediction methods for seamless integration with experimental approaches will be intensified.

Broader Impacts and Workforce Development: GlycoMIP employs multiple approaches to train the next generation of glycomaterials researchers in accelerated glycomaterials development. Undergraduate students are trained through the GlycoMIP-associated, NSF-funded GlycoTREE Research Experiences for Undergraduate program, currently in its second year. GlycoMIP-affiliated graduate students and postdocs work in multidisciplinary teams and receive feedback on their research in monthly, team-wide work-in-progress meetings. GlycoMIP holds annual education events, such as Summer Schools and Short Courses, open to U.S. researchers of all career stages and research institutions. To increase diversity within the glycomaterials workforce and user community, GlycoMIP offers grant programs to facilitate participation by researchers from non-R1 and HBCU/MSI institutions in the GlycoMIP user program and education/training events.

Data Management and Knowledge Sharing: The GlycoMIP data sharing platform, glycodata.org, launched in February of 2023, has been accessed more than 8,500 times from locations around the globe **(Figure 2)**.

Figure 2. Global map of GlycoData.org visitors.

Advancing Along the Materials Development Continuum and Partnerships to Translation: GlycoMIP engages with industry through its user program, education/training program, and External Advisory Committee with the goal to establish several long-term collaborations with industry partners.

Publications and References

1. E. Kucukdeger, and B. N. Johnson, *Closed-loop controlled conformal 3D printing on moving objects via tool-localized object position sensing,* Journal of Manufacturing Processes ***89***, 39-49 (2023). DOI**:** 10.1016/j.jmapro.2023.01.020
2. J. Zhang, Y. Liu, D. Chandra Sekhar.P, M. Singh, Y. Tong, E. Kucukdeger, H. Y. Yoon, A. P. Haring, M. Roman, Z. J. Kong, and B. N. Johnson, *Rapid, autonomous high-throughput characterization of hydrogel rheological properties via automated sensing and physics-guided machine learning,* Applied Materials Today ***30***, (2023). DOI**:** 10.1016/j.apmt.2022.101720
3. E. Kucukdeger, Y. Zhang, J. Zhang, Y. Liu, X. Jia, and B. N. Johnson, *Automated characterization of macroscale tissue 3D spatial material properties via robotically-directed impedimetric sensing,* IEEE Transactions on Automation Science and Engineering, 1-13 (2023). DOI**:** 10.1109/TASE.2023.3279338
4. Y. Liu, J. Zhang, Y. Zhang, H. Y. Yoon, X. Jia, M. Roman, and B. N. Johnson, *Accelerated engineering of optimized functional composite hydrogels via high-throughput experimentation,* ACS Applied Materials and Interfaces, (2023). DOI**:** 10.1021/acsami.3c11483
5. J. Zhang, P. Srivatsa, F. H. Ahmadzai, Y. Liu, X. Song, A. Karpatne, Z. Kong, and B. N. Johnson, *Reduction of biosensor false responses and time delay using dynamic response and theory-guided machine learning,* ACS Sensors ***8(11)***, 4079-4090 (2023). DOI**:** 10.1021/acssensors.3c01258
6. J. Zhang, P. Srivatsa, F. H. Ahmadzai, Y. Liu, X. Song, A. Karpatne, Z. J. Kong, and B. N. Johnson, *Improving biosensor accuracy and speed using dynamic signal change and theory-guided deep learning,* Biosensors and Bioelectronics ***246***, (2024). DOI**:** 10.1016/j.bios.2023.115829
7. S. K. Singh, K. King, C. Gannett, C. Chuong, S. Y. Joshi, C. Plate, P. Farzeen, E. M. Webb, L. K. Kunche, J. Weger-Lucarelli, A. N. Lowell, A. M. Brown, and S. A. Deshmukh, *Data driven computational design and experimental validation of drugs for accelerated mitigation of pandemic-like scenarios,* Journal of Physical Chemistry Letters ***14(42)***, 9490-9499 (2023). DOI**:** 10.1021/acs.jpclett.3c01749
8. S. K. Singh, A. T. Sose, F. Wang, K. K. Bejagam, and S. A. Deshmukh, *Data driven discovery of MOFs for hydrogen gas adsorption,* Journal of Chemical Theory and Computation ***19(19)***, 6686-6703 (2023). DOI**:** 10.1021/acs.jctc.3c00081
9. J. Chung, J. Li, A. I. Saimon, P. Hong, and Z. Kong, *Predicting the stereoselectivity of chemical reactions by composite machine learning method,* Scientific Reports ***14(1)***, 12131 (2024). DOI**:** 10.1038/s41598-024-62158-0

Accelerated Discovery of Sustainable Bioplastics: Automated, Tunable, Integrated Design, Processing and Modeling

Lead Investigator: Eleftheria Roumeli, eroumeli@uw.edu
Participating Institutions: University of Washington, Duke University, University of Vermont, University of Colorado at Boulder.
Source of Support: NSF-DMREF
Website: none
Keywords: Algal bioplastics, High throughput, Machine learning, Feature extraction, Molecular dynamics

Project Scope

This program aims to develop a new class of fully biodegradable bioplastics with performance comparable to commodity plastics, produced sustainably. We use high-throughput methods to analyze processing, spectroscopic, and morphological features, identifying key factors controlling the transformation of biological matter to bioplastics. Molecular dynamics simulations and high-fidelity experiments will validate these findings. Comprehensive structure and property measurements, alongside high-throughput FEA, will form a second dataset for developing structure-property relationships. An integrated machine learning framework will then optimize the bioplastic processing from whole organisms.

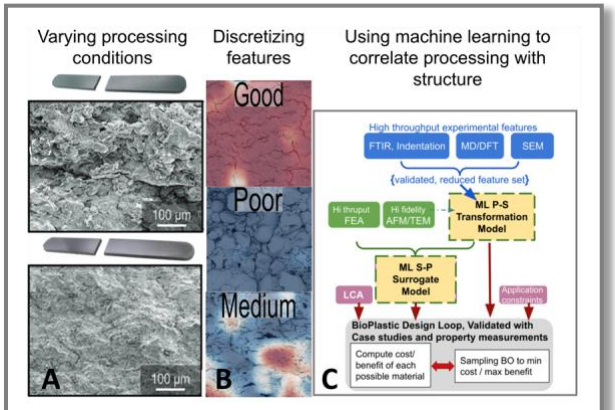


Figure. A) Photographs of algal bioplastics processed using different conditions and their corresponding microstructure images using SEM. B) Examples of classification if different bioplastic samples based on their microstructural features using GLCM and VAEs. C) Flow chart depicting the application of different data types to develop and verify multiple ML models designed to connect first processing and structure, and then structure to properties for algal bioplastics.

Relevance to MGI

This project aligns with the 2021 MGI strategic plan by combining high-throughput data capture, multiscale modeling, and machine learning to understand and optimize the bioplastic formation process from biomatter. Our key hypothesis is that thermomechanically-driven reactions, kinetically-driven structure formation, and microstructurally-controlled properties govern this transformation. To validate this, we have created an analogue system with representative building blocks (long and short carbohydrates, proteins, and lipids). We have analyzed the structure, mechanical properties, and molecular interactions, and developed an MD model to elucidate intermolecular interactions. Additionally, we have initiated a machine learning (ML) model for image recognition of critical structural features, enabling classification linked to the structure-property relationships.

This iterative process enhances each component of the research: synthesis and processing inform characterization, which in turn refines computational models. This synergy accelerates materials discovery and development, contributing to a fundamental knowledge base for designing bioplastics with specific, desired properties, thus advancing the goals of MGI.

Technical Progress

To understand the fundamental mechanisms governing the formation of biomatter plastics, we have developed both experimental and simulated analogues for algal bioplastics. Traditional chemical analyses (like Fourier transform infrared spectroscopy (FTIR)) of algal bioplastics are constrained by the compositional complexity of natural tissues and cells. To circumvent this limitation, we constructed simplified physical and computational biomatter models comprising pure carbohydrates, proteins, and lipids. The analogue composites are designed not for practical application but to enhance the fundamental understanding of biomatter plastics.

By varying the ratios of each component, we formed materials that emulate the composition of algal bioplastics. Evaluation of scanning electron microscopy (SEM) images and mechanical performance isolated the role of each class of macromolecule. Spectroscopic analyses, such as FTIR, reveal that cohesion in biomatter analogues is dictated by protein aggregation during thermomechanical processing. MD simulations support these findings, suggesting that changes in protein conformation and intermolecular hydrogen bonding induce the formation of a cohesive, proteinaceous matrix. These simulations also corroborate experimental measurements, emphasizing the crucial role of hydrogen bonding and self-assembly among small molecules.

In addition, we are developing a ML model for image recognition of critical microstructural features, enabling classification linked to the structure-property relationships. We have successfully extracted useful features from the SEM images that represent the quality of the self-bonding through both the texture extraction method Gray-Level Co-occurrence Matrix (GLCM) and Variational AutoEncoders (VAEs) without relying on the labeled bonding conditions. Moreover, we have evaluated the extracted features using a dimension reduction (DR) method for data visualization called Pairwise Controlled Manifold Approximation (PaCMAP). We observe clear separations among samples with qualitatively "good", "medium" and "poor" bonding within this DR projection.

Future Plans

We plan to further advance the understanding and optimization of biomatter plastics through a series of targeted experimental and computational efforts. Currently we are focusing on the development of a high-throughput manufacturing tool designed to scan a wide range of transformation conditions. This tool will enable us to systematically generate a large volume of data very rapidly. Simultaneously, we will collect more high-fidelity data using Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). These techniques will provide detailed insights into the nanoscale structure and morphology of our bioplastic analogues and help to implement finite element analysis (FEA).

Moreover, we will further expand our analogue model system to include the effects of carbohydrate molecular weight and branching, as well as the structure of lipids, on the properties of the bioplastic. This will involve evaluating our model system through MD simulations, complemented by targeted experiments to validate the simulation results.

The data generated will contribute to a comprehensive ML framework for the design and manufacturing of high-performance, sustainable bioplastics. Our integrated approach will provide the necessary insights to develop bioplastics that meet the performance standards of traditional plastics while offering significant environmental benefits.

Broader Impacts and Workforce Development

The project is a collaboration across three institutions and multiple research groups, and has already significantly contributed to the education and training of the next generation of scientists and engineers. Currently, 5 Ph.D. students, 3 undergraduate students, and XX master's students are actively engaged in this interdisciplinary research, learning the principles and applications of the Materials Genome Initiative (MGI) in a highly collaborative environment. The implementation of this research is also being utilized as a tool to better communities in eastern Washington. The development of sustainable materials derived from natural, local resources like algae, have the opportunity to foster sustainable economic development for indigenous communities. To that end, an ongoing partnership has been developed with the Chief Leschi Schools of Puyallup, Washington.

Data Management and Open Access

This project has augmented the MaterialsMine Knowledge Graph ontology to connect to additional terms that can describe the composition and processing of hot pressed spirulina bioplastics. We will use these terms to curate existing and new bioplastics data.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The data from this project will be integrated into an open source data resource, MaterialsMineTM. We have been improving the ontology to accommodate the terms appropriate for this work, and developing new data ingestion approaches that will make it easier to accommodate this work. Ultimately this work will enable a deeper understanding of how to optimize the properties of bioplastics made directly from biomatter.

Publications and References

1. I.R. Campbell, Z. Dong, P. Grandgeorge, A.M. Jimenez, E.R. Rhodes, E. Lee, S. Edmundson, S.V. Chinmayee, K.G. Sprenger, E. Roumeli, The role of biomolecular building blocks on the cohesion of biomatter plastics, Under revision

Demystifying the role of excipients in whole viral vaccines

Lead Investigators: Sapna Sarupria, sarupria@umn.edu. Sarah L. Perry, perrys@engin.umass.edu. Caryn L. Heldt, heldt@mtu.edu.
Participating Institutions: University of Minnesota, University of Massachusetts Amherst, Michigan Technological University
Source of Support: NSF-DMREF
Website: https://www.umass.edu/perry/DMREF/
Keywords: vaccine, excipients, amino acids, thermostabilization, active learning

Project Scope

Viral vaccines require refrigeration throughout their distribution cycle. Excipients are added to formulations to enhance vaccine stability, with the hypothesis that they stabilize viral vaccines by creating a favorable solvent environment. Our objective is to develop a framework integrating experiments, modeling, and machine learning to identify molecular features that confer stability. We aim to discover and optimize excipient mixtures for vaccine formulations, focusing on their effects on water structure and stability of viral components. Success will be measured by predicting and validating stabilizing excipients through experimental and computational methods.

Relevance to MGI

Understanding the subtleties of how the molecular structure of excipients affects water structure and thus modulates the stability of biomolecules, such as proteins and viruses, remains a grand challenge with significant implications for both the biophysical and biochemical communities. To address this, we aim to develop a framework that integrates experimental and computational approaches to identify molecular features that impart stability and discover complex excipient mixtures for enhanced vaccine thermal stabilization. Our research combines experiments on individual excipients' ability to stabilize model protein lysozyme and porcine parvovirus (PPV) against thermal denaturation with molecular simulations exploring excipient effects on a model hydrophobic polymer, lysozyme, and a part of the capsid. By training machine learning (ML) models to predict stabilizing excipients for lysozyme, we establish a feedback loop where experimental data informs computational models, and these models, in turn, guide further experiments. This approach fosters a synergistic interaction between synthesis, characterization, and theory, leading to the design of excipient formulations.

Technical Progress

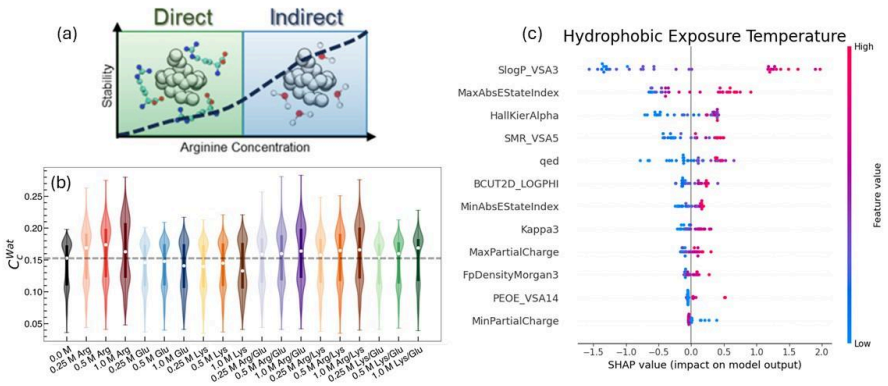


Figure 1: (a) Concentration-dependent direct-indirect stabilization mechanism switch observed in arginine solutions.[1] (b) Closeness centrality among water molecules in excipient solutions indicates that increased connectivity in arginine-containing solutions enhances the stability of a model linear hydrophobic polymer.[2] (c) SHAP analysis of an RF model trained on lysozyme in excipient experiments reveals that lysozyme stabilization is influenced by a specific hydrophobicity range in the excipients.

We started our investigations by focusing on arginine. Arginine has been reported to have unique stabilizing and denaturing properties in different contexts. Through molecular dynamics (MD) simulations of coarse-grained polymers, lysozyme, and part of the PPV capsid, we proposed a novel explanation for arginine effects based on competing direct and indirect

mechanisms (Fig. 1a).[1] Additionally, mechanistic studies on excipient mixtures of arginine, glutamate, and lysine revealed the solvent network's role in synergistically enhancing stability in certain combinations (Fig. 1b).[2]

The thermal stability studies on the effect of arginine revealed that high concentrations of arginine in liquid state destabilize PPV. Similar results were obtained by MD simulations of a charged polymer. The direct interaction between positively charged arginine and the negatively charged residues on the surface of the virus is believed to be the reason for the destabilizing effect of arginine. Lysine, another cationic amino acid, exhibited similar destabilization behavior, which indicates the dominance of charge interactions over hydrophobic interactions in the thermostability of PPV. Strikingly, arginine destabilized lysozyme at low concentrations but was stabilizing at high concentrations. Furthermore, both lysine and glutamate were stabilizing at all concentrations, suggesting that stability may be due to a convolution of effects.

For high-throughput screening of excipient combinations, we trained Random Forest and Gaussian Process Regression models to predict stability measures of lysozyme and PPV in diverse excipient solutions. While our models accurately identified stabilizing excipients for lysozyme, we are still working on improving their performance for PPV. Further analysis using Shapley additive explanation (SHAP) highlighted the significant impact of excipient hydrophobicity in lysozyme stabilization (Fig. 1c).

Future Plans

Future steps involve performing experiments on an additional small model cationic protein (thaumatin), green fluorescent protein (GFP) as a model anionic protein, and apoferritin as a larger anionic protein that could help bridge the length scales between protein and virus. We will also study an additional virus (minute virus of mice, MVM) to broaden our study of how the surface features of viruses interact with excipients and drive changes in stability. We are also developing a multi-fidelity model to assess the usefulness of other protein experiments in predicting the stability of a new protein or virus.

Broader Impacts and Workforce Development

Community outreach has focused on using 3D-printed and/or hand-crafted viruses to demonstrate different aspects of viruses and vaccines. The first project connected kinetics and thermodynamics to capsid assembly, and was accompanied by a discussion of the challenges associated with the formulation of vaccines and other biologics. A second project involved the creation of crafting instructions to create the capsid of the human rhinovirus using needlepoint and plastic canvas. Each PI has leveraged local high school outreach programs as a platform to describe the importance of chemistry to the stability of viral vaccines. The viruses have been printed, and multiple demonstrations have been completed. Altogether, four graduate students are involved and are being trained in this team. Two graduate students gave a talk at the 2024 APS March Meeting held in Minneapolis, MN.

Data Management and Open Access

Data and code will be available on our DMREF website upon publication

Advancing Along the Materials Development Continuum and Partnerships to Translation

The goal of this project is to provide a computational framework to increase the discovery of excipients for viral vaccines. This framework will be available for industrial partners to use to help narrow their experimental space and increase the stability and time to market in the area of formulation. As we get closer to developing the framework, we will reach out to industrial partners to explore their interest in the tool.

Publications and References

1. J.W. Zajac, P. Muralikrishnan, I. Tohidian, X. Zeng, C.L. Heldt, S.L. Perry, S. Sarupria, *Flipping Out: Role of Arginine in Hydrophobic Interactions and Biological Formulation Design,* arXiv:2403.11305v1 (2024)
2. J.W. Zajac, P. Muralikrishnan, C.L. Heldt, S.L. Perry, S. Sarupria, *Impact of Co-Excipient Selection on Hydrophobic Polymer Folding: Insights for Optimal Formulation Design,* arXiv:2407.00885 (2024)

Design of energy storage pseudocapacitive materials

Lead Investigator: Philippe Sautet, sautet@ucla.edu
Participating Institutions: University of California Los Angeles, Stanford University
Source of Support: NSF-DMREF
Website: none
Keywords: Energy storage, Pseudocapacitive properties, descriptors, transition metal oxides

Project Scope

Electrical energy storage is essential to the energy transition and to the reduction of greenhouse gas emissions. Capacitors represent a class of electrical energy storage devices that can be charged very quickly. The realization of capacitors that could store a large amount of electrical energy could have an enormous impact on energy storage for the electricity grid, for electric mobility solutions, and for consumer electronics. This project aims at designing novel capacitive materials that can greatly increase the energy storage of electrochemical capacitors with fast charging and discharging. The project's societal impact lies in its contributions towards the decarbonization of the transportation sector which accounts for 29% of all greenhouse gas emission in the United States today.

Relevance to MGI

The scientific approach will be based on a material design loop including experiments and modeling in order to define the features of pseudocapacitive materials enabling high storage ability, in the spirit of the MGI and on a large computational screening of prospective materials to obtain candidates that will be tested experimentally.

The aim of this research program is to tightly combine experimental and computational methods to identify a new generation of electrochemical energy storage materials based on pseudocapacitance, defined as a charge storage mechanism which uses fast and reversible surface or near surface redox reactions, and to construct a prototype device integrating the energy storage materials. While the underlying principles of pseudocapacitance are understood, there is currently no ability to predict or design materials that display pseudocapacitive behavior. A double design loop is proposed. The first one will operate at the atomic scale and will combine first principle electronic structure calculations with synthesis and testing. It will provide thermodynamics and kinetic information to the second level of design that will involve optimization of energy storage device configurations, combining continuum modeling and experimental synthesis and characterization. From this approach, an energy storage device will be demonstrated based on the developed pseudocapacitive materials. The project will bring fundamental understanding of the factors governing pseudocapacitive material performance and provide practical guidelines for the design of high performance energy storage materials and devices.

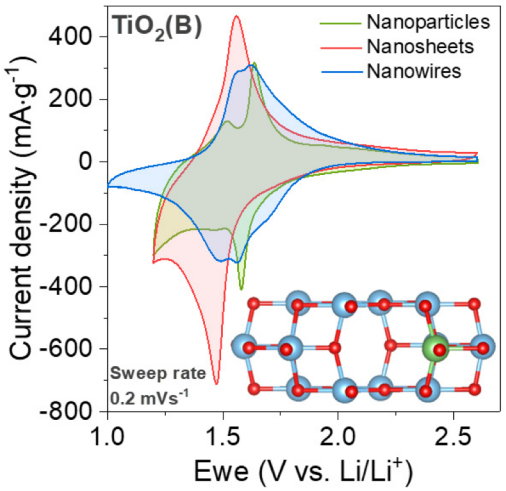


Figure 1: Cyclic voltammetry of Li^+ intercalation into TiO_2(B) nanoparticles, nanowires and nanosheets. The pseudocapacitive response varies according to the different crystal facets exposed to the electrolyte interface. Insert: calculated structure (Li green).

Technical Progress

Since the start of the project in Fall 2023, we have defined the lists of core real materials and of initial attributes for the database. We have also prepared a structure for that database. We have initiated the construction of the data by using an example material, TiO_2(B), a bronze polymorph of titanium dioxide. We

synthesized it in three morphologies, studied the details its pseudocapacitive properties, and performed first-principles calculations of its bulk and surface structure and of Li intercalation processes. This activity has also allowed us to train post-doctoral and graduate students on the methods and to precisely define the characterization and computational approaches, both at the atomic scale and at the mesoscopic scale. The approach has been extended to other oxides including *T*-Nb_2O_5, MoO_2 and VO_2(B) to start building the required database, and will soon include dichalcogenides such as TiS_2 and MoS_2. We have planned out the synchrotron experiments including high resolution diffraction and absorption spectroscopy to characterize structure and chemistry of synthesized materials in the database.

Future Plans

The first objective of the project is to complete an initial version of the real system database, to evaluate the capacitive behavior and to determine all the attributes for each system. This will demand a large effort of synthesis, characterization and computation. Indeed, some of the attributes are obtained by experiments, while others are better obtained from simulations. As soon as a reasonable amount of data is obtained we will start to evaluate various machine learning models first to select discriminative attributes, called descriptors, and then to build a performance-structure model. From the **computational screening of an extended materials database**, we will obtain a number of candidate materials, distinct from the pseudocapacitive solids known today, and the best ones in terms of energy density and potential range will be synthesized and evaluated.

A second task will consist of modeling interfacial and transport phenomena in porous electrodes and optimizing the geometry of the energy storage device at the macroscopic scale. This task will be based on our state-of-the-art multiphysics model accounting for ion electrodiffusion in the electrolyte, finite ion size, electrical double layer formation, redox reactions, near-surface ion intercalation, and resistive losses. Transport properties (e.g., ion diffusion coefficient, electrode conductivity) and redox reaction rate constants will be obtained from our atomic scale simulations or from the literature. The model will be rigorously validated against electrode and/or device experimental characterization. The final task will be to construct the device based on incorporating pseudocapacitive materials.

Broader Impacts and Workforce Development

The project integrates research and training of three Ph.D. students and one post-doctoral researcher at the frontier of materials design and discovery. Each student will have a major topic and a minor topic, thus leading to a new generation of student with broad knowledge of both experimental and computational materials science. The project will also be used as a platform for the training of undergraduate students in topics related to energy storage and modeling. We will take advantage of the existing infrastructure at UCLA and Stanford University to attract talented, ethnically and culturally diverse undergraduate student populations in cutting-edge research. With the development of a web-based simulation app, the graduate students supported by the program will participate in our successful outreach program that enables high school science teachers to bring exciting science into their classrooms.

Data Management and Open Access

The database is being defined and constructed. It will be shared broadly after publication.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Despite the potential significance of pseudocapacitive materials for high energy/high power electrical energy storage, the approach used to date to identify appropriate materials has involved the tedious process of synthesizing and characterizing materials one-by-one. In this light, it is hardly surprising that relatively few pseudocapacitive materials have been identified. The current project aims at the rational design of pseudocapacitive materials from a MGI approach and should accelerate the discovery of high energy and high power storage devices.

Publications and References

No peer-reviewed publications associated with this project at the moment.

DMREF/Collaborative Research: Designing Mutable Metamaterials with Photo-Adaptive Meta-Atoms

Lead Investigator: M. R. Shankar, ravishm@pitt.edu.
Participating Institutions: M. R. Shankar (U. Pitt), M. Brongersma (Stanford), H. Noh (Stanford), K. Dayal (Carnegie Mellon), R. Lipton (Louisiana State)
Website: none.
Keywords: Active Metastructures, Machine Learning, Liquid Crystal Elastomers, Inverse Design, Plasmonics

Project Scope

The goal of this research is to design and fabricate adaptive, topologically optimized polymer-composite plasmonic metastructures, whose interaction with light can be modulated using light itself. A focus will be on endowing plasmonic structures with mechanical adaptivity using photochromic switching in a macromolecular network with which they are composited. The driving hypothesis is that plasmonic structures can couple photons into photomechanically responsive polymers on which they are resident. This photomechanical response controls the topology of the plasmonic structures and enables dynamic optical responses (beam steering, wavefront shaping).

Relevance to MGI

This research integrates analytical models by Lipton, computational methods from Brongersma to design libraries of nanoscale plasmonic structures that couple photons with photochromic switches. These forward models map the optical responses to the adaptive topology of the nanostructures. In parallel, inverse models by Noh and Dayal utilize machine learning to design nanostructures for optical functionalities. The models are used to design an experimental thrust to fabricate plasmonic structures on photoresponsive liquid crystal elastomers (LCE). This effort involved the development of new strategies for compositing inorganic materials among molecularly programmed soft matter using a range of emerging patterning and nanofabrication techniques. Characterization of the optical properties can then validate computational methods and refine the machine learning based approaches for inverse designs. The iterative coupling between theory and experiments (Figure 1) accelerates the discovery of active plasmonic structures, which can offer device level functionalities to manipulate light using light itself.

Technical Progress

The project developed a suite of techniques for fabricating nm-scale films of molecularly ordered LCE on a range of substrates. These include quartz, glass, Au and Au/Ti multilayers. One approach involved the development of a blade coating technique to create thin layers of LCE monomer mixtures on substrates (e.g., quartz). The focus was on utilizing canonical liquid crystalline monomers (e.g. RM82) in combination with optimized mole fraction of chain extenders, which also provide functionality as a chain transfer agent (e.g., 1,4 benzenedimethane thiol). Optimized compositions allowed for the blade coating of thin films. The monomer films ordered on alignment layers were polymerized to create the LCE on a range of substrates. In parallel, a soft lithography-based approach was developed for creating nanometer scale LCE films on gold substrates. This approach utilized a ~ T magnetic field to enforce molecular alignment by exploiting the anisotropic diamagnetic susceptibility of the reactive mesogens. Optimized compositions were developed to inherit the alignment, while allowing for patterning of thin layers using soft lithography. The samples were decorated with nanoparticles to explore the effect of the responsiveness of LCE substrates on the scattering response. Nanostencil lithography was developed for solvent free patterning of nanostructures on polymer films using SiN_x hard masks. These masks were placed directly on substrates to transfer ultrafine features through evaporation of metal layers. The experimental campaign was complemented by analytical models

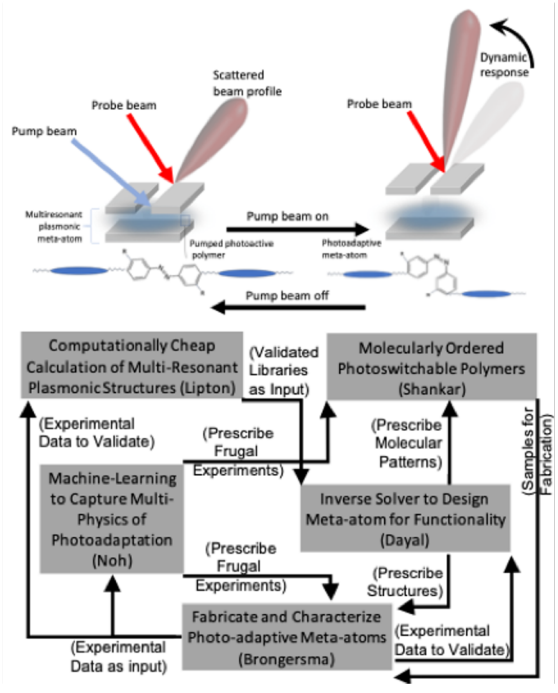


Figure 1. Integrating computational, analytical and machine learning approaches with experimental methods to accelerate the discovery of photo adaptive metastructures.

to understand the effect of geometry and material properties on the interaction of multicomponent impedance surfaces with incident electromagnetic radiation. A new analytic model for plasmonic particles patterned on very thin film coatings was established. It modeled the metal on film layer as an effective impedance layer sensitive to periodic localized plasmon resonances. The forward models were used to train a neural network to capture the essential features of the optical response as a function of geometry and material properties. The physics informed deep learning model developed alleviates the issue of non-interpretable result that is often encountered in case of predictions with deep learning models.

Future Plans

The frameworks for modeling the interaction between light and the nanostructures, as well as the development of fabrication techniques will be brought to bear for realizing designs of the active metastructures.

Broader Impacts and Workforce Development

This project supports two PhD students at the University of Pittsburgh, who are developing methods for creating nanostructured thin films with optimized photoactive compositions. Carnegie Mellon University has hired one PhD student to work on the machine learning. This student is co-advised by Prof. Noh and Dayal. Stanford has hired one PhD student to work on the nanofabrication of the plasmonic structures and characterization of the photomechanical responses. Lousiana State University has recruited one PhD student to develop the analytical models. Students supported by the grant at the Pittsburgh and Louisiana were also embedded at the Air Force Research Laboratory via the AFRL/DMREF supplement. This allowed their exposure to research in a non-academic setting, while broadening the network of collaborations.

Data Management and Open Access

Our team is committed to sharing the codes on open-source platforms and disseminating the results via publications and conference presentations.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The experimental and theoretical breakthroughs positioned the PIs to accelerate the translation of the designs into practical applications. These include an array of follow-up grant applications and the pursuit of system design opportunities to demonstrate the optical adaptivity.

Publications and References

The following papers and presentations acknowledge support from this grant:

1. Gao, Junfeng, et al. Advanced Materials Technologies 7.5 (2022): 2100979.
2. Clement, Arul, et al. Mechanics Letters 47 (2021): 101362.
3. Wang, Zhijie, and M. Ravi Shankar. Diamond and Related Materials 121 (2022): 108763.
4. Robert Lipton and R. Perera. Journal of Differential Equations 332 (2022): 1-49.
5. Li, Wei, Robert Lipton, and Matthias Maier. Proceedings of the Royal Society A 477.2256 (2021): 20210609.
6. Adili, Abiti, et al. Proceedings of the Royal Society A 478.2263 (2022): 20220194.
7. Sarkar, Sulagna, et al. "Physics-Guided Machine Learning Framework for Simultaneous Inverse Design and Optical Response Prediction of Photonic Metamaterials", SIAM Annual Meeting (2022).
8. Sarkar, Sulagna, et al. "Physics based Machine Learning for inverse design of metasurfaces", Mechanistic Machine Learning and Digital Twins for Computational Science, Eng. & Tech.: An IACM Conference (2021).
9. Lipton, R., et. al. European Society of Applied and Industrial Mathematics: Math- emtical Modeling and Numerical Analysis. 56.5 (2022): 1483-1519.
10. Giudici, A., et al. Europhysics Letters 140.3 (2022): 36003.
11. Wang, Zhijie, and M. Ravi Shankar. Diamond and Related Materials 130 (2022): 109482.
12. Jha, Prashant K., Timothy Breitzman, and Kaushik Dayal. Archive for Rational Mechanics and Analysis 247.2 (2023): 29.
13. LoGrande, Kevin, M. Ravi Shankar, and Kaushik Dayal. Soft Matter 19.45 (2023): 8764-8778.
14. Sarkar, Sulagna, et al. Advanced Photonics Research 4.12 (2023): 2300158.
15. Khandagale, Pratik, et al. Physical Review E 107.6 (2023): 064501.
16. Khandagale, Pratik, et al. *Physical Review E* 109.4 (2024): 044501.
17. Shrivastava, Ankit, et al. Mathematics and Mechanics of Solids 27.7 (2022): 1336-1357.
18. Jha, Prashant K., et al. Journal of Applied Mechanics 90.2 (2023): 021003.
19. Yang, Jianfeng, M. Ravi Shankar, and Hao Zeng. Nature Communications 15.1 (2024): 4684.

Programmable Design, Synthesis, and Forensics of Soft Materials

Lead Investigator: Sergei S. Sheiko, sergei@email.unc.edu
Participating Institutions: University of North Carolina at Chapel Hill and Carnegie Mellon University
Source of Support: NSF-DMREF
Website: none
Keywords: Polymer networks, programmable properties, forensics.

Project Scope

The project pursues the development of programmable soft materials by integrating molecular codes, automated synthesis, and forensic structural analysis. Structurally encoding physical properties and retroactively deciphering network structure from mechanical response is a major intellectual challenge. Theory and computer simulations define a set of codes, encompassing the composition, architecture, and property evolution in time. These descriptors are implemented into an AI-guided in-flow synthesis, wherein real time characterization and feedback loops enable iterative property optimization. The design-by-architecture approach will accelerate the synthesis of elastomers, gels, and thermoplastics with tailored combinations of orthogonal properties encoded in molecular structure.

Relevance to MGI

The stated goal aligns with NSF 10 Big Ideas: Growing Convergence Research and Harnessing the Data Revolution. Specifically, this DMREF project will converge polymer chemistry, soft matter physics, and data science to build a foundation for an open-source Big Data search engine that will provide protocols for molecularly programmable design and synthesis of soft materials. This engine will include an AI-driven and forensically verified library of molecular codes, quantitative inputs for software-enabled continuous flow synthesis, and protocols for high throughput materials characterization.

Technical Progress

The ability to synthesize elastomeric materials with programmable mechanical properties is vital for soft matter applications. Due to inherent complexity of hierarchical structure-property correlations in polymer networks, the application of conventional theory-based, so-called Human Intelligence (HI) approaches becomes increasingly difficult. By synergistically combining HI and AI tools, we developed a design strategy, which allows precise

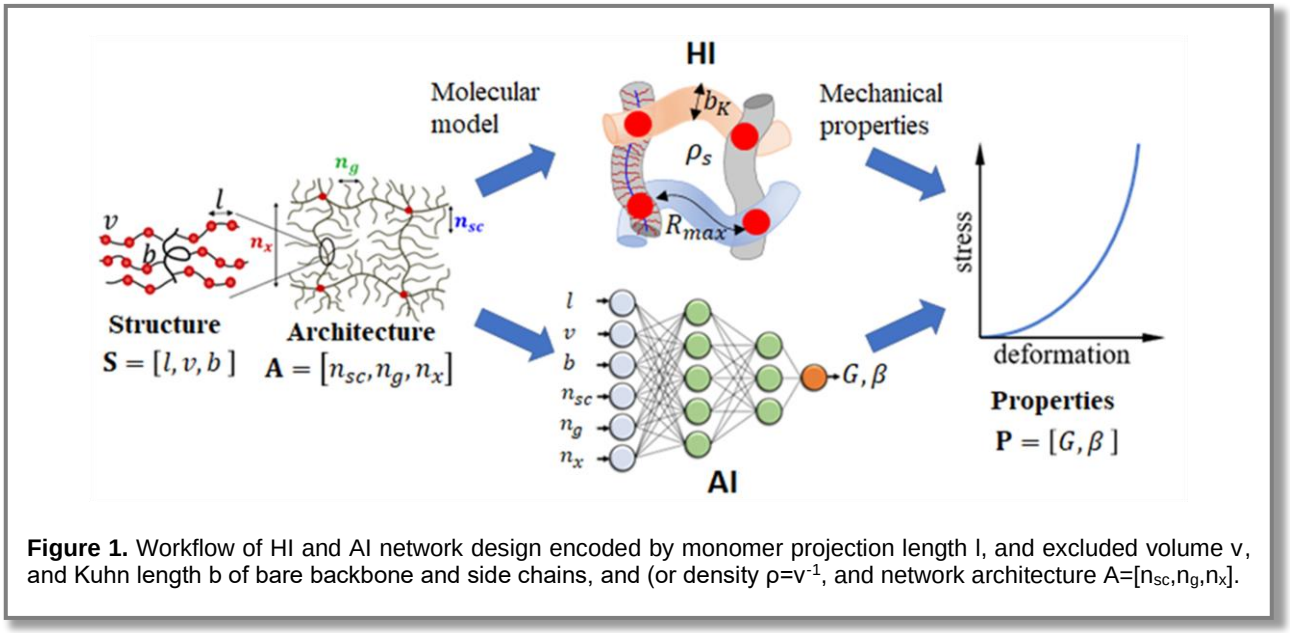


Figure 1. Workflow of HI and AI network design encoded by monomer projection length l, and excluded volume v, and Kuhn length b of bare backbone and side chains, and (or density $\rho=v^{-1}$, and network architecture $A=[n_{sc},n_g,n_x]$.

encoding of mechanical properties with network architectural parameters (**Figure 1**). Implementing a multi-layer feedforward artificial neural network (ANN), we took advantage of model-predicted structure-property cross-correlations between coarse-grained system code including chemistry specific characteristics, network architecture, and network equilibrium mechanical properties. The ANN was trained by minimizing the mean-square error with Bayesian regularization to avoid overfitting using a data set of experimental stress-deformation curves of networks with brush-like strands of poly(n-butyl acrylate), polyisobutylene, and polydimethylsiloxane having structural modulus $G < 90$ kPa and $0.01 \leq \beta \leq 0.9$. The trained ANN predicts network mechanical properties with 95% confidence.

Future Plans

Leibfarth and Dobrynin are developing a method for real-time characterization of molar mass that operates at high concentrations, where polymerization is typically conducted, providing instantaneous feedback on reaction progress. The closed-loop of theoretical and experimental efforts will enable real-time synthetic adjustment to accelerate materials optimization and scale-up. In parallel, the Matyjaszewski group will synthesize libraries of macromolecules with varied mass, architecture, and composition to validate the predicted universal viscosity representation. Sheiko and Dobdrynin are working on merging AI and forensics methodology for non-invasive evaluation of network topology, which is vital for verification of the structural codes.

Broader Impacts and Workforce Development

Implementing digital codes in soft matter design will drive new synthetic pathways, stimulate new physical models, and catalyze fundamental shifts in various technologies, including personalized medicine, soft robotics, and sustainable materials fabrication. We collaborate with the Ackland Museum of Art to educate students on the connection between Materials Science concepts and Art in different cultures across human history. Building on this knowledge, participating students will create artwork merging Materials Science and Art, publicly displayed during the "Second Fridays" at Ackland. In addition, our team will develop the CREATE (Consider, Read, Elucidate the hypothesis, Analyze and interpret data, and Think of the next Experiment) method to give undergraduate students creative ownership of the research design and execution, as well as build an inclusive environment. Finally, several innovative programs will support the inclusivity culture in materials research: (i) reverse site visits by the DMREF team to HBCUs and MSIs to advertise center activities and recruit broad participation, and (ii) a partnership with the Chancellors Science Scholars program to increase the participation of undergraduate students from URGs.

Data Management and Open Access

Each research thrust will produce data domains, including (i) HI/AI-generated and forensics-verified structural codes for targeted properties, (ii) reactivity ratios for predicting comonomer sequences, and (iii) calibration curves for in-situ molecular characterization. Specifically, we create a Data Bank of architectural codes that mimics the mechanical response of biological tissues from ultra-soft fat tissue to highly resilient skin. The data will be cross-correlated to build a fully integrated platform for automated materials design based on prediction-implementation-verification of structure-property correlations. The UNC is building a centralized FAIR data depository, which will allow for the data sets, ML models, codes and training data sets generated by the DMREF team members to be freely accessible. Currently the data are available from https://tarheels.live/dobryningroup/data-request/. These data include: (i) computer simulation data (input files for LAMMPS, simulation trajectories, tables with analyzed data sets); (ii) experimental data (synthetic protocols, molecular characterization, thermal and mechanical data).

Advancing Along the Materials Development Continuum and Partnerships to Translation

Closed-loop programming of material properties, automated synthesis, and structural forensics is pivotal to accelerating and enhancing the efficiency of materials discovery. This approach is particularly vital for technologies that require an array of soft materials with customized combinations of distinct physical properties such as stiffness, damping, swelling, and adhesion. In collaboration with AbbVie, our group is working on the development of soft tissue implants for reconstructive surgery. The first batch of materials is currently being tested at the AbbVie research facility. If successful, licensing and joint product development will be considered.

Publications and References

1. A.V. Dobrynin, A. Stroujkova, M. Vatankhah-Varnosfaderani, S.S. Sheiko “Coarse-Grained Artificial Intelligence for Design of Brush Networks.” *ACS Macro Lett*. **12**, 1510-1516 (2023). DOI: 10.1021/acsmacrolett.3c00479
2. E.A. Nikitina, E. Dashtimoghadam, S.S. Sheiko, D.A. Ivanov, “Bottlebrush Elastomers with Crystallizable Side Chains: Monolayer-Like Structure of Backbones Segregated in Intercrystalline Regions.” *Polymers* **16**, 1-11 (2024). DOI: 10.3390/polym16020296
3. E.K. Neidhart, M. Hua, Z. Peng, V. Bhat, F. Vashahi, S.S. Sheiko, C. Wang, B.A. Helms, F.A. Leibfarth “C–H Functionalization of Polyolefins to Access Reprocessable Polyolefin Thermosets.” *J. Am. Chem. Soc*. 145, 27450-27458 (2023). DOI: 10.1021/jacs.3c08682
4. S.A. Kostrov, J.H. Marshall, M. Maw, S.S. Sheiko, E.Y. Kramarenko “Programming and Reprogramming the Viscoelasticity and Magnetic Response of Magnetoactive Thermoplastic Elastomers.” *Polymers* **15**, 1-11 (2023). DOI: 0.3390/polym15234607
5. C.J. Wang, F. Vashahi, I. Moutsios, A.Z. Umarov, D.I. Ivanov, G.G. Ageev, Z. Wang, A.V. Dobrynin, S.S. Sheiko, S.S. “Bottlebrush Hydrogels with Hidden Length: Super-Swelling and Mechanically Robust.” *Adv. Funct. Mater*. Submitted 06/21/2024.

National High Magnetic Field Laboratory

Facility: National High Magnetic Field Laboratory
Facility Director: Kathleen Amm, ammk@magnet.fsu.edu
Facility Deputy Director (or Associate Director): Eric Palm, palm@magnet.fsu.edu
MGI PI Meeting Participant in 2024: Theo Siegrist, siegrist@magnet.fsu.edu,
David Butcher, dbutcher@magnet.fsu.edu
Source of Support: NSF-DMR-2128556, NSF-DMR-1644779, NSF-DMR-1844191
Website: https://nationalmaglab.org
Keywords: High Magnetic Fields, ICR, EMR/NMR, topology, Fermi surface study

The National High Magnetic Field Laboratory

The National High Magnetic Field Laboratory (NHMFL) provides access to static and pulsed high magnetic fields to the community of users. The magnetic field is a thermodynamic variable that affects the Gibbs free energy of a system, and therefore allows tuning of ground state. With electrons coupling strongly to the magnetic field, probing and tuning the electronic ground state of a system/material is possible. The NHMFL has the expertise to probe the electronic ground state of materials and provides a suite of measurement tools and capabilities. The NHMFL is home to scientists and engineers who develop measurement tools for electronic properties of materials, that include low temperatures and high magnetic field behavior. Large amounts of data are acquired that need to be stored and processed.

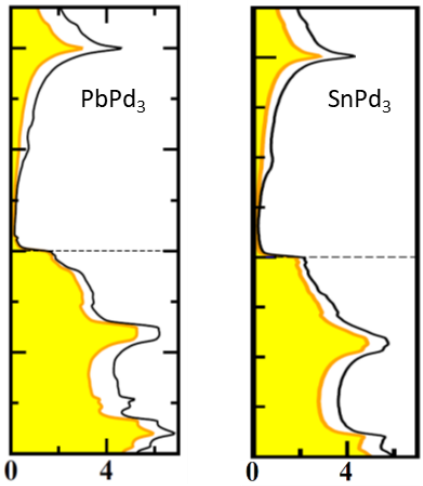
The Ion Cyclotron Resonance facility (ICR) analyzes the mass of molecular compounds that are present in complex mixtures including biological, environmental, and petroleum samples with ultrahigh resolving power and precision. The number of observations in this case is very large, requiring an extensive data management strategy.

Relevance to MGI

The characterization of materials is an important part of the MGI strategic plan. Curated data of high quality is required for the feedback loop to work. The NHMFL has developed tools that ensure high data quality as well as provide user support and training in the use of these tools.

The NHMFL Theory Winter School as well as the Experimental Summer School both serve to train students and postdocs in theory and experimental techniques.

Example: Flat bands at the Fermi level promise high thermoelectric response due to large dN/dE values. DFT calculations identified the primitive cubic $AuCu_3$-type $PbPd_3$ and $SnPd_3$ as promising candidates, where the Fermi level coincides with a flat band between the Γ and the X point in reciprocal space. We set out to synthesize and grow single crystals using the Bridgman technique to test these materials and the prediction based in DFT computations. The determination of the Fermi surface as well as the thermoelectric properties of the compound serve to assess the feasibility of the materials.



Technical Progress

The NHMFL as a national user facility aims at serving a large user base. Established users have an excellent understanding of the application process and do have a well-functioning network of user support scientists to rely on. For groups without prior experience, an on-boarding process has been implemented that includes the measurements of initial data that can be used for magnet time applications. For this, SCM5 and SCM6, a Quantum Design MPMS and Quantum Design PPMS are available to measure magnetic susceptibility and electronic transport properties, as well as thermodynamic properties. If needed, additional characterization tools such as optical microscopy and spectroscopy, electron microscopy, as well as diffraction methods are available.

Development of measurements methods and new measuring capabilities are ongoing projects that address the needs of the user community. Integration of different measurement techniques provide unique opportunities to study material properties under extreme conditions (e.g. high magnetic fields, pressure, low temperatures) and provide feedback to computational methods. Examples are the combination of diffraction with high magnetic fields, 1.5GHz NMR techniques, thermal transport, contact-less electronic transport measurements, measurements of very small samples processed with focused ion beams (FIB).

Future Plans

New and improved measurement techniques will be made available to users on an ongoing basis. In-house research serves to develop new materials measurement capabilities. Data management techniques are under development to ensure FAIR data management for all products of research.

Broader Impacts and Workforce Development

The theory winter school and the experimental summer school for graduate students and postdocs develop the workforce in materials theory and materials characterization. Furthermore, the NHMFL research faculty, FAMU and FSU affiliated faculty train graduate students and postdocs in a collaborative environment, where they often interact with external users and assist in user support. In addition, the Applied Superconductivity Center (ASC) is leading efforts in developing high T_c superconductors coils for potential application in research devices as well as fusion reactors. This is reflected in the high demand of graduates of ASC by external companies.

Data Management and Open Access

The NHMFL has adopted a data management plan and policies that require users to make data, publications, and other products of research publicly available after an embargo period. The ability of the NHMFL to enforce practices that make data FAIR is limited as the responsibility for data stewardship ultimately lies with users. However, the MagLab is developing new cyberinfrastructure that will facilitate the automated capture of FAIR data and metadata.

The ICR facility recently established a collaboration with the Computer Science Department at Florida State University to develop workflows for the exploitation of facility data. An important facet of this project is the development of a database solution designed for long-term storage and public availability of facility data while enabling its use for artificial intelligence and machine learning applications. After development and implementation in the ICR facility, this solution will be applied to other NHMFL facilities.

Advancing Along the Materials Development Continuum and Partnerships to Translation

Materials and device developments at the NHMFL are ongoing. The expertise in magnet design is made available to outside customers (example: NHMFL - ORNL and NHMFL – Cornell collaborations). Development of Bi2212 superconducting round wire is an ongoing process at ASC. Such wire will allow easier-to-realize coil designs. Research into precipitation hardened copper alloys is carried out to improve the lifetime of copper coils and their mechanical behavior under high stress condition during operation.

Publications and References

Butcher, D. S. et al. Cybersecurity in a Large-Scale Research Facility—One Institution's Approach. Journal of Cybersecurity and Privacy 3, 191–208 (2023). doi.org/10.3390/jcp3020011

DMREF: Engineering the On-the-Fly Control of 3-D Printed Block Bottlebrush Assemblies via Dynamic Bonds and Materials Processing

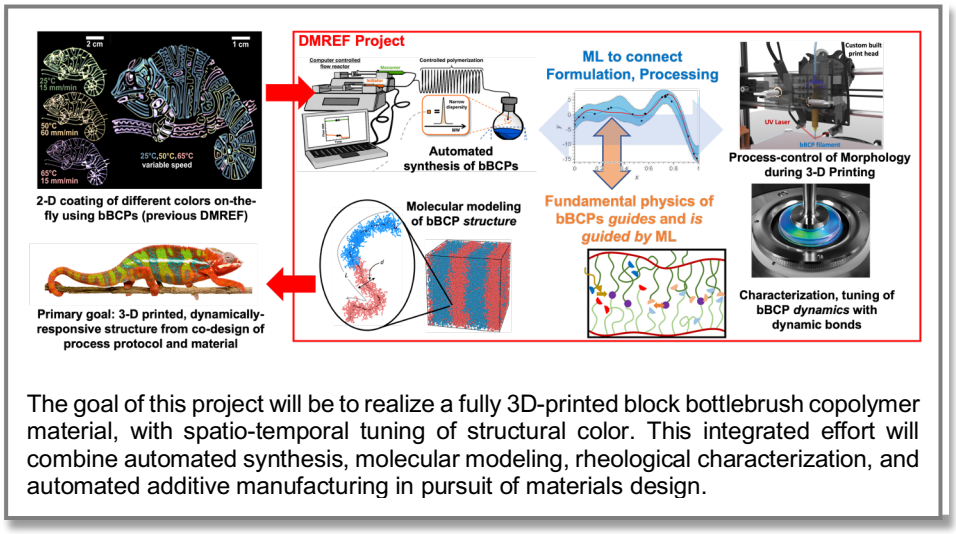
Lead Investigator: Charles E. Sing, cesing@illinois.edu
Participating Institutions: University of Illinois at Urbana-Champaign
Source of Support: NSF-DMREF
Website: non.
Keywords: Polymer architecture, self-assembly, additive manufacturing, dynamic bonds, structural color.

Project Scope

This DMREF program will establish the fundamental science and design rules for harnessing the versatility of process-directed, 3-D printed bottlebrush block copolymer (bBCP) materials. Processing variables such as flow rate can manipulate and pattern self-assembled morphologies at the molecular level. Bottlebrush block copolymers are an ideal platform because they self-assemble rapidly, and they can be synthesized with a wide range of architectures and dynamic interactions that provide a large parameter space. We will efficiently explore this parameter space via an experimental/computational approach that is informed by machine learning; we seek to engineer processing-dependent assembly by controlling molecular shape and interactions.

Relevance to MGI

This research program uses a combined approach of synthesis, characterization, modeling, and machine learning to realize material-processing approaches for advanced additive manufacturing. This is intended as an integrated approach to materials design, utilizing the combined expertise of the PIs. The overall goal will be to co-design a bottlebrush block copolymer material, chemical functionality, and a 3-D printing process to exhibit on-the-fly, spatially-varying morphologies. To this end, Guironnet synthesizes molecules with precise architectures, to be used and characterized by Diao and Rogers. Rogers will develop insights into rheology and structure, accompanied by molecular simulation from Sing, that will provide insight into printing performed by Diao. Automated synthesis and formulation from Guironnet, along with printing and characterization of assembled structures by Diao will provide the foundations for automated printing schemes developed in collaboration with Maruyama at AFRL. This will be used to identify interesting parameter regimes in synthesis, and focus the attention of fundamental studies by Rogers and Sing; these physical insights inform automated printing to make it generally adaptable to 3-D printing processes. Over half of the 19 papers published in the previous iteration of this DMREF project were multi-PI efforts, evidence of a highly-integrated research team.



Technical Progress

This project has resulted in several key research accomplishments: (1) The development of new synthesis methods to increase the variety of block bottlebrush polymers, such as the ability to synthesize soft blocks, end-functionalized side-chains with dynamic bonds, various grafting densities and larger length-scale molecules. (2) Characterization using SAXS and rheology showed how timescales of crosslinking and self-assembly can be controlled to tune kinetically-trapped morphologies. (3) Synthesized bBCPs that can be photocrosslinked were

incorporated into solution coating printing processes, giving full on-the-fly control over structural color. (4) A coarse-grained molecular model of bottlebrush structure used to show how solution processing leads to these changes in structural color, (5) New 'implicit side-chain' models were developed to understand bottlebrush assembly in semidilute and melt systems, (6) Rheological measurements and models were developed to connect yielding and gelation/curing physics, which is important for material printing, and (7) Initial efforts to establish autonomous printing schemes were successful. We have established a comprehensive picture of bBCP solution assembly, and demonstrated that processing could be used to modulate structural color on-the-fly.

Recent progress has centered around further engineering crosslinking and solvent-control to tune bBCP assembly in and out of equilibrium. This includes (1) developing synthetic methodologies to increase the chemical versatility of bBCPs we can consider, (2) using coarse-grained models to simulate the properties of shape-defined bottlebrushes in the melt state, (3) determine protocols for the melt assembly of bottlebrush systems, with the goal of obtaining long-ranged order needed for 3-D printing, (4) refining an autonomous printing scheme that can rapidly characterize structural color for changing printing conditions, and (5) characterizing the yielding rheology of bottlebrush assemblies, important for 3-D printing. We have begun to address the coupled challenges of understanding molecular assembly versus processing versus bottlebrush synthesis, and how these relate to material properties and molecular structure.

Future Plans

The next steps for this project are to systematically understand the assembly and mechanical properties of melt bottlebrush assemblies and their incorporation into an autonomous printing setup. Intermediate efforts will focus on (1) extending coarse-grained modeling approaches to contend with melt bottlebrush assembly, including shape-defined bottlebrushes, (2) using recovery rheology techniques to understand the connection between structural color and mechanical properties, (3) establishing automated and versatile syntheses to incorporate dynamic bonds and molecular 'shape' into bottlebrush assemblies, and (4) incorporating the connection between structural color, morphology, and processing conditions into an automated structural color characterization scheme. Longer-term efforts will be centered around integrating fundamental studies of bBCPs into an automated materials discovery scheme, combining automated synthesis and printing, as well as fundamental physical modes and insights, to design a versatile set of bBCPs that can exhibit dramatic and controllable structural color changes.

Broader Impacts and Workforce Development

The educational impact of this DMREF project comes in part from the collaboration between four PIs with complementary backgrounds. Cross-disciplinary knowledge was gained by students, who will benefit from a broader education that will prepare them for STEM careers. This program has played a role in training 10 graduate students, 2 postdoctoral researchers, and several undergraduate students. We also participate in outreach efforts, developing programming for the Girls' Adventures in Mathematics, Engineering, and Science (GAMES) camp, the St. Elmo Brady STEM Academy, and using expertise in 3-D printing for a 'CCCR-Champaign County COVID Relief projects to make 3-D printed face masks and respirators.

Data Management and Open Access

This project will generate a large amount of data composed of computational code, outputs from simulations, synthesis characterizations, and rheological and scattering data. We facilitate long-term stewardship of our data by adhering to the FAIR (findable, accessible, interoperable, and reusable) guiding principles. Both theoretical/computational and experimental data will be archived and hosted on data repositories when possible, using standard file formats that will be made available upon publication.

Publications and References

1. S. Jeon, Y.L. Kamble, H. Kang, J. Shi, M.A. Wade, B.B. Patel, T. Pan, S.A. Rogers, C.E. Sing, D. Guironnet, Y. Diao, *Direct-ink-write Cross-linkable Bottlebrush Block Copolymers for On-the-fly Control of Structural Color.* Proc. Natl. Acad. Sci. USA **121,** e2313617121 (2024).
2. B.B. Patel, T. Pan, Y. Chang, D.J. Walsh, J.J. Kwok, K.S. Park, K. Patel, D. Guironnet, C.E. Sing, Y. Diao, *Concentration-Driven Self-Assembly of PS-b-PLA Bottlebrush Diblock Copolymers in Solution*, ACS Polymers Au. DOI: 10.1021/acspoolymersau.1c00057 (2022).
3. T.P. Pan, S. Dutta, Y. Kamble, B.B. Patel, M.A. Wade, S.A. Rogers, Y. Diao, D. Guironnet, C.E. Sing, *Materials Design of Highly Branched Bottlebrush Polymers at the Intersection of Modeling, Synthesis, Processing, and Characterization*, Chem. Mater. **34**, 1990 (2022).
4. A. Deptula, M.A. Wade, S.A. Rogers, R.M. Espinosa-Marzal, *Charge-Induced Structural Changes of Confined Copolymer Hydrogels for Controlled Surface Morphology, Rheological Response, Adhesion, and Friction,* Adv. Funct. Mat. **32,** 2111414 (2022).
5. J. Shi, S.A. Rogers, *The Benefits of a Formalism Built on Recovery: Theory, Experiment, and Modeling,* J. Non-Newt. Fluid Mech. **321,** 105113 (2023).
6. Y.L. Kamble, D.J. Walsh, D. Guironnet, *Precision of Architecture-Controlled Bottlebrush Polymer Synthesis: A Monte Carlo Analysis,* Macromolecules, **55,** 10255-10263 (2022).
7. S. Dutta, C.E. Sing, *Brownian Dynamics Simulations of Bottlebrush Polymers in Dilute Solution Under Simple Shear and Uniaxial Extensional Flows,* J. Chem. Phys. **160,** 044901 (2024).

Collaborative Research: DMREF: GOALI: Discovering Materials for CO_2 Capture in the Presence of Water via Integrated Experiment, Modeling, and Theory

Lead Investigator: Randall Q. Snurr, snurr@northwestern.edu
Participating Institutions: Northwestern University, University of South Alabama, NuMat Technologies
Website: none
Keywords: Carbon capture, nanoporous materials, metal-organic frameworks, separations, adsorption

Project Scope

Carbon capture and sequestration are widely viewed as essential tools, along with other technologies, to keep atmospheric CO_2 levels from rising further. This project focuses on developing new materials for selective adsorption of CO_2 versus N_2. Metal-organic frameworks (MOFs) are a promising class of materials for carbon capture due to their modular building-block synthesis, which allows for targeted tuning of material properties and for an almost unlimited number of potential MOFs. A primary emphasis of this project is the effect of water on CO_2/N_2 selectivity and CO_2 capacity. The main goal is to develop integrated simulation, theoretical, and experimental methods for understanding the effect of water on CO_2/N_2 separations in MOFs and to use these tools to speed up the discovery of new adsorbents for CO_2 capture and related separations.

Relevance to MGI

This project contributes to the development of new strategies for creating adsorbent materials with programmable structures by precisely combining preassembled building blocks (i.e., MOF nodes, organic linkers, ions, and functional groups). In particular, we focus on a few MOF platforms that can be systematically tuned by changing the organic linkers, introducing extra-framework anions and cations, and restructuring the MOF nodes. These "platform" MOFs are chosen from families of MOFs known to exhibit excellent stability. Optimization of MOF synthesis will be accelerated by the use of robotic synthesis tools coupled with machine learning algorithms. Molecular simulation is used to test new proposed material variations and provide molecular-level insights into observed behavior. The simulation models are validated against adsorption data collected by our team, including multicomponent adsorption measurements, which are extremely scarce in the literature. All simulated and experimental adsorption data will be placed in publicly accessible databases and will be used to assess the accuracy of methods for predicting mixture behavior from single-component adsorption isotherms. For the most promising materials, we perform single-crystal X-ray studies of molecular siting and arrangements in the pores.

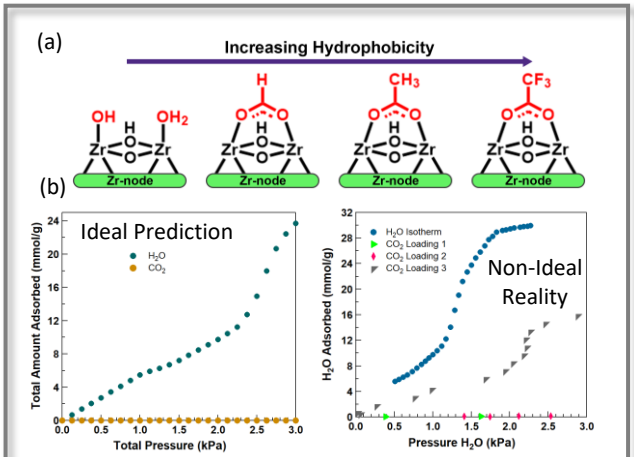


Figure 1. Water is an ever-present component in flue gas streams, and dehumidification of the flue gas stream is cost-prohibitive. Therefore, one concept explored in this project is how MOF hydrophobicity affects CO_2/N_2 selectivity and CO_2 working capacity for the materials in (a). This project also explores how the theory predicting H_2O/CO_2 co-adsorption on the materials shown in (a) does not match the experimentally observed behavior shown in (b). Understanding why the experimentally observed behavior differs from the expected behavior is critical to discovering new materials.

Technical Progress

CALF-20, a Zn-triazolate-based metal–organic framework (MOF), is one of the most promising adsorbent materials for CO_2 capture in the literature. However, competitive adsorption of water severely limits its performance when the relative humidity (RH) exceeds 40%, limiting the potential implementation of CALF-20 in practical

settings where CO_2 is saturated with moisture, such as postcombustion flue gas. We have recently introduced [8] three newly designed MOFs related to CALF-20, denoted as NU-220, CALF-20M-w, and CALF-20M-e that feature hydrophobic methyltriazolate linkers. Inclusion of methyl groups in the linker was proposed as a strategy to improve the uptake of CO_2 in the presence of water. Notably, both CALF-20M-w and CALF-20M-e retain over 20% of their initial CO_2 capture efficiency at 70% RH─a threshold at which CALF-20 shows negligible CO_2 uptake. Grand canonical Monte Carlo simulations reveal that the methyl group hinders water network formation in the pores of CALF-20M-w and CALF-20M-e and enhances their CO_2 selectivity over N_2 in the presence of a high moisture content. Moreover, calculated radial distribution functions indicate that introducing the methyl group into the triazolate linker increases the distance between water molecules and Zn coordination bonds, offering insights into the origin of the enhanced moisture stability observed for CALF-20M-w and CALF-20M-e relative to CALF-20. This straightforward design strategy has afforded more robust sorbents that can potentially meet the challenge of effectively capturing CO_2 in practical industrial applications.

Additionally, mixed-gas adsorption measurements have revealed unexpected behaviors on a Zr-based MOF functionalized with trifluroacetic acid. When water was preadsorbed on the MOF, and a subsequent CO_2 adsorption isotherm was measured, the CO_2 adsorption isotherm was slightly reduced, providing a somewhat expected outcome. However, when CO_2 was adsorbed first and then an H_2O adsorption isotherm was measured, no significant H_2O adsorption capacity was observed. The near complete loss of water adsorption capacity was observed when only a trace amount of CO_2 was preadsorbed. The results show that unexpected, non-state function adsorption equilibrium behaviors can result from the dynamic behavior of MOFs, which may lead to counterintuitive adsorption data compared to traditional materials with a static adsorbent structure. These results have important implications when applying these types of MOFs industrially using techniques such as pressure or temperature swing adsorption, which are of particular interest for direct air capture or post-combustion capture of CO_2. For example, slightly different gas phase compositions could produce significant changes in adsorption capacity, or changes in cyclic working capacity may be observed.

Future Plans

In the final year of the project, we continue to explore variants of CALF-20, including the effect of framework flexibility on their CO_2 and water uptake. We are also investigating MOFs with extra-framework anions as another platform for materials that can selectively adsorb CO_2 over N_2 in the presence of water.

Broader Impacts and Workforce Development

The project contributes to the education of 4 PhD students in an interdisciplinary project, as well as several post-docs. Summer undergraduate students have been recruited through a program that brings students from underrepresented groups to our campuses. Web-based education activities will reach a wider audience.

Data Management and Open Access

Simulation results will be placed in a searchable, public database, including relevant metadata, such as details about the force field parameters used to generate the data, so that all calculations are fully reproducible. The adsorption data are stored in a standardized JSON format that is interoperable with the NIST adsorption database. By making all this data more easily accessible, we hope to facilitate new data mining and machine learning studies on these materials, leading to new insights on adsorption in MOFs.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The project aims to discover new materials for carbon capture by using “platform” materials that can be tuned in a systematic way. Importantly, these materials can be explored computationally to accelerate the discovery process. The proposed research has the potential to contribute to the mitigation of CO_2-driven climate change. This work may also lead to nanoporous materials that may be useful in applications such as chemical separations, gas storage, sorption-based cooling, and water purification. The involvement of a co-PI from NuMat Technologies helps identify “show stoppers” and ensures that the team is working on industrially relevant problems.

Publications and References

1. J. Liu, R. Anderson, K.M. Schmalbach, T.R. Sheridan, Z. Wang, N.M. Schweitzer, A. Stein, N.A. Mara, D. Gomez Gualdron, J.T. Hupp, *Dual-Functional Modification to Enhance Water Stability of Mesoporous Zirconium Metal–organic Frameworks*, J. Mater. Chem. A **10**, 17307 – 17316 (2022). doi: https://doi.org/10.1039/D2TA03851J
2. K.M. Fahy, M.R. Mian, M.C. Wasson, F. Son, T. Islamoglu, O.K. Farha, *Exchange of coordinated carboxylates with azolates as a route to obtain a microporous zinc–azolate framework*, Chem. Commun. **58**, 4028 – 4031 (2022). doi: https://doi.org/10.1039/D2CC00925K
3. T.M. VanOursouw, T. Rottiger, K.A. Wadzinski, B.E. VanderWaal, M.J. Snyder, R.T. Bittner, O.K. Farha, S.C. Riha, J.E. Mondloch, *Adsorption of a PFAS Utilizing MOF-808: Development of an Undergraduate Laboratory Experiment in a Capstone Course*, J. Chem. Educ. **100,** 861 – 868 (2023). doi: https://doi.org/10.1021/acs.jchemed.2c00910
4. T.M. Rayder, F. Formalik, S.M. Vornholt, H. Frank, S. Lee, M. Alzayer, Z. Chen, D. Sengupta, T. Islamoglu, F. Paesani, K.W. Chapman, R.Q. Snurr, O.K. Farha, *Unveiling Unexpected Modulator-CO_2 Dynamics within a Zirconium Metal–Organic Framework*, J. Am. Chem. Soc. **145**, 11195 – 11205 (2023). doi: https://doi.org/10.1021/jacs.3c01146
5. S. Kancharlapalli, R.Q. Snurr, *High-Throughput Screening of the CoRE-MOF-2019 Database for CO_2 Capture from Wet Flue Gas: A Multi-Scale Modeling Strategy*, ACS Appl. Mater. Interfaces **15**, 28084 – 28092 (2023). doi: https://doi.org/10.1021/acsami.3c04079
6. Z. Chen, K.O Kirlikovali, L. Shi, O.K. Farha, *Rational design of stable functional metal–organic frameworks*, Mater. Horiz. **10**, 3257 – 3268 (2023). doi: https://doi.org/10.1039/d3mh00541k
7. F. Formalik, K. Shi, F. Joodaki, X. Wang, R.Q. Snurr, *Exploring the Structural, Dynamic, and Functional Properties of Metal-Organic Frameworks through Molecular Modeling*, Adv. Funct. Mater. 2308130 (2023). doi: 10.1002/adfm.202308130
8. X. Wang, M. Alzayer, A.J. Shih, S. Bose, H. Xie, S.M. Vornholt, C.D. Malliakas, H. Alhashem, F. Joodaki, S. Marzouk, G. Xiong, M. Del Campo, P. Le Magueres, F. Formalik, D. Sengupta, K.B. Idrees, K. Ma, Y. Chen, K.O. Kirlikovali, T. Islamoglu, K.W. Chapman, R.Q. Snurr, O.K. Farha, *Tailoring Hydrophobicity and Pore Environment in Physisorbents for Improved Carbon Dioxide Capture under High Humidity*, J. Am. Chem. Soc. 2024, **146**, 3943 – 3954 (2024). doi: https://doi.org/10.1021/jacs.3c11671
9. M.A. Khoshooei, X. Wang, G. Vitale, F. Formalik, K.O. Kirlikovali, R.Q. Snurr, P. Pereira-Almao, O.K. Farha, *An active, stable cubic molybdenum carbide catalyst for the high-temperature reverse water-gas shift reaction*, Science **384**, 540 – 546 (2024). DOI: 10.1126/science.adl1260

GOALI: Physics-Informed Artificial Intelligence for Parallel Design of Metal Matrix Composites and Their Additive Manufacturing

Lead Investigator: Aaron Stebner, aaron.stebner@gatech.edu
Participating Institutions: Georgia Institute of Technology, University of Utah, University of Michigan, Air Force Research Laboratory
Source of Support: NSF-DMREF
Keywords: Metal Matrix Composites, Process-Structure-Property Relations, Additive Manufacturing, Machine Learning, Physics-based Modeling.

Project Scope

The scope of this project is to create physics informed artificial intelligence for parallel design of metal matrix composites and their additive manufacturing techniques. Currently, materials design consists of a series of independent approaches at different length-scales along the process-structure-property (PSP) pipeline. These include microstructural models, data-driven and physics-informed experiments, and experimental verification. This project seeks to create hierarchical materials development pipelines that aggregate these disparate length scales in autonomous data pipelines. We aim to create algorithms for data feature engineering, nested PSP models, and automated data feature mapping toward accelerating the development of metal matrix composites.

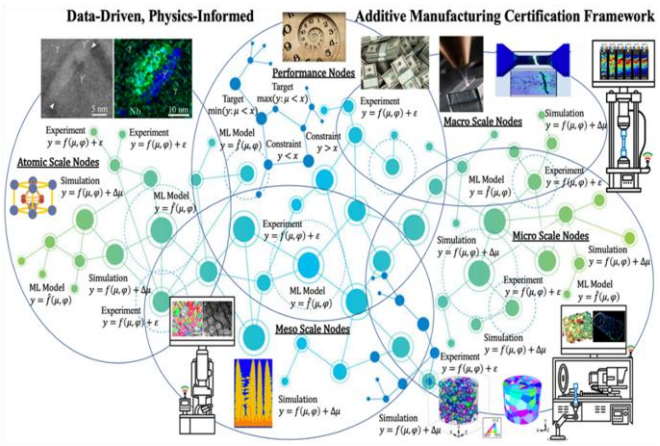


Figure 1. We aim to treat each of the disparate pieces of materials development as "nodes" that need to be understood and aggregated to create workflows that span between nodes and enable autonomous workflows.

Relevance to MGI

We are creating frameworks to integrate MGI's core objectives with the following metal matrix composite (MMC) goals in mind: eliminating cracking and tearing, speeding build times, refining grains, and creating desirable mechanical properties. We integrate experimental verification of MMC aluminum models, aiming to create a closed feedback loop to inform future experiments. Object-oriented algorithms are also being created to facilitate the aggregation of these disparate nodes.

Technical Progress

In the modeling sector, we have implemented a new work-hardening formulation coupled with triaxiality-based continuum damage mechanics to an existing large-strain elasto-viscoplastic fast Fourier transform (LS-EVPFFT) code. The new constitutive formulation models the hardening behavior of MMCs by considering several mechanisms that are each a function of particle reinforcement composition, namely, a Hall-Petch effect, a geometric mismatch effect, a difference in thermal expansions effect, and an Orowan effect. The recently augmented framework captures the global stress-strain responses of aluminum MMCs measured experimentally, while enabling the correlation between fracture-initiation location and microstructure-neighborhood attributes. Thus far, the model has been tested on a subset of test data for verification and proof of concept. With the increase in current data that is in the process of being provided by the experimental partners on this project, new microstructures based on EBSD data have been created using DREAM.3D and SPPARKs. In addition, the physics-based models of incorporating ceramic particle synthesis and effects into process-structure models through laser absorption, keyhole evolution, metal evaporation and recoil pressure, and particle motion also continues to be calibrated using 1000-series aluminum MMC samples printed on powder-bed system.

In the experimental and characterization sector, we have been utilizing electron microscopy techniques to characterize the microstructure of samples of A1000 ceramic-reinforced MMC printed on the EOS M280 powder-bed system. Interestingly, we have observed that the reactive additive manufacturing (RAM) process used in these samples did not complete. Electron backscattered maps in the 3 direction planes (normal, rolling, and transverse) have shown the decreasing grain size and texture with increasing inoculant concentration in addition to the bimodal grain structure along the build direction with elongated grains spanning the center of the melt pool and smaller, refined grains along the melt pool boundaries. With the grain sizes reaching sub-micron diameters at the 2 and 10% inoculant concentrations, the EBSD indexing quality was significantly reduced. Transmission electron microscopy images show dislocation pileups at the grain boundaries and particulates.

From the algorithm development sector, we have developed frameworks of distinct test artifact levels considering the underlying process maps and the changes between them required to link the relevant process-structure-property relations. We are in the process of developing in-depth pseudocode of material processing parameter space searches using abstraction to enable new modules to be "plug and play" as new models and sensors are validated and calibrated. A1000 ceramic inoculated powder for directed energy deposition (DED) systems has also been acquired as a test-case for algorithm development.

Future Plans

Future plans include continuation of the tensile testing of the powder-bed fusion generated A1000 with ceramic reinforcement tensile bars. Sample processing of the single-track experiments to validate melt pool modeling is also in progress for the upcoming months. For sample characterization sample characterization, we will investigate the dislocation and particulate interactions after mechanical testing in addition to the matrix-particle interfaces in regions of high strain. These regions of interest will be determined by in situ DIC-EBSD testing which is currently in progress. The goal is to understand how the microstructure evolves under tensile loading, but also to implement a multiscale study in which we investigate how the particulates are playing a role in the mechanical behavior. We will continue to update the models to study the effects of defects using the LS-EVPFFT modified modeling framework. Specifically, studying the effect of pores and agglomerations along with microstructural features will help identify causes of varying ductility within MMCs. Within this study, thresholds for critical defects will be explored. We will also continue to develop algorithms and the necessary decision metrics, aggregate test results from disparate tests. We will be verifying these workflows on a A1000 with 10% ceramic RAM inoculants that we aim to print on a laser directed energy deposition system.

Broader Impacts and Workforce Development

Due to the high cost of designing MMCs, high-fidelity models that accurately capture the effects on the hardening, damage, and critical defect impact are required. The ability to simulate 3D grain texture from 2D EBSD will also enable the simulation of mechanical properties. Autonomous algorithms will also enable high-throughput samples, and the increase in data will allow us to have better data-driven models. These advances will create tools for more accessible MMC manufacturing. The project also continues to provide professional development for the DMREF Ph.D. students through biweekly meetings, conference opportunities, and experimental collaboration, as well as research opportunities for undergraduate students.

Data Management and Open Access

This project implements FAIR data practices using collaborative platforms and aggregate data processing. We implement AFRL's HyperThought platform where datasets are extracted, structured, and related, all via API. The data are related with a process model, followed by procedural generation of model attributes and relational structure. These file/object process models are then made available through REST API or through a user interface in HyperThought cloud instance.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We will enable partnerships through software such as HyperThought and DREAM.3D, in which DMREF students will become developers and users for HyperThought and DREAM.3D userbase. We will also seek to take advantage of AFRL internships for our DMREF graduate students. Previously, a 2-day HyperThought hackathon was held with the goals of project advancement and collaboration, and we aim to hold more in the future. Additionally, our industry partnerships such as Elementum3D will provide historical techno-economic data on existing MMC feedstock development cycles.

Publications and References

1. Spear, A. D. *Material Modeling in Additive Manufacturing*. In Additive Manufacturing Design and Applications, p60-66 (2023). ASM International. https://doi.org/10.31399/asm.hb.v24A.a0006988
2. Tan, W., & Spear, A. Multiphysics Modeling Framework to Predict Process-Microstructure-Property Relationship in Fusion-Based Metal Additive Manufacturing. *Accounts of Materials Research*, 5(1), 10-21 (2024): https://doi.org/10.1021/accountsmr.3c00108

Establishing a molecular interaction framework to design and predict modern polymer semiconductor assembly

Lead Investigator: Natalie Stingelin, natalie.stingelin@mse.gatech.edu
Participating Institutions: Georgia Institute of Technology, North Carolina State University
Source of Support: NSF-DMREF
Website: none
Keywords: polymer semiconductors, molecular interactions, phase behavior, solution assembly, thermomechanics

Project Scope

The objective of this project is to establish a framework that accurately captures the molecular interactions and secondary and tertiary structures of modern semiconducting polymers and develop descriptors that dictate and classify assembly of these complex macromolecules. The vision is to advance a knowledge platform toward the predictable and controlled self-assembly of multicomponent plastic semiconducting inks that lead to targeted device properties.

Relevance to MGI

This DMREF project we will advance fundamental knowledge related to materials design and processing through advanced testing methodology, theory, computation and leveraging machine learning and data mining towards accelerated materials discovery in the organic semiconductor field. The project is divided into four interwoven research thrusts that focus on specific aspects of the semiconducting polymer assembly puzzle: Thrust 1: Computational Modelling, Thrust 2: Solution Assembly, Thrust 3: Thermal Transitions, and Thrust 4: Solid-State Structure. Thrust 1 is fully theory driven, while Thrust 2-4 are run in a close feedback loop between experiments, theory, and machine learning activities, with Thrust 2 especially using ML/AI engines for phase space mapping and accelerated discovery. The team will employ density functional theory and molecular dynamics (MD) simulations that capture secondary structures that may be formed by a given polymer (primary structure) and that will influence solution assembly, thermal transitions as well as solid-state structure. Complimentary to these efforts, research will include experimental data on solutions (UV-vis absorption and PL spectra, SAXS patterns) that provide insights in secondary (chain conformations) and tertiary structures (aggregation) in the liquid state. In addition, films will be studied, with fast calorimetry, DMA, VASE, GIWAXS, NEXAFS and UV-vis spectroscopy to gain information into local/segmental relaxations, phases present, phase transitions and larger-scale packing order. The use of advanced ML techniques will allow us to extract non-trivial correlations within the obtained data. Such correlations will then be used for further materials design cycles.

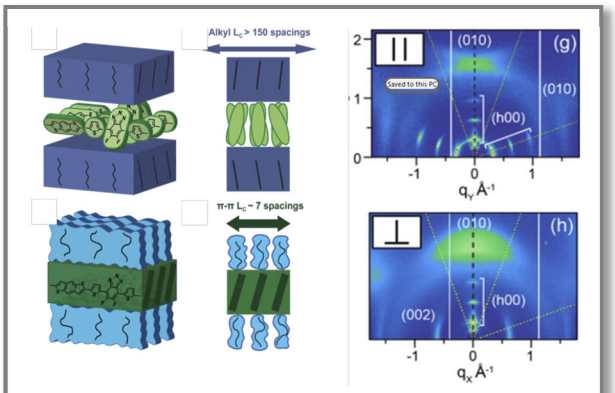


Figure. Left, competing ordering of the backbone and side-chains of a conjugated polymers.[1] Right, GIWAXS pattern of oriented PBnDT-FTAZ polymer film showing unique packing characteristics under specific processing conditions.

Technical Progress

The projected started in October 2023. We have begun experiments at national laboratory X-ray beamlines for detailed process-structure-property relationships. We have begun developing advanced molecular dynamic simulations that reinforce the experimentally observed packing structure. We have initial results that show how differences in molecular structure impact accessible packing microstructure.

Future Plans

We plan to conduct in-situ small angle neutron scattering experiments of polymer semiconductors to understand assembly pathways and aggregate packing arrangements. We will employ machine learning approaches to accelerate mapping the solution phase space of these systems. Overall, data-rich environments such as ML/AI-guided modeling and solution SAXS/WAXS/UV-vis spectroscopy are complemented with in-depth studies of phase behavior and molecular packing of solid films of candidate materials identified by modeling and solution characterization. The application of ML is necessary to identify systems and conditions that yield the most informative structure-function insights, and avoids producing redundant information in the vast and complex multi-parameter phase-space and this accelerates experimental and computation efficiency. The MD simulations will use the information gathered to develop accurate interaction energies. Thermomechanical measurements will be conducted to also gain insight into molecular interaction energies and related to processing schemes to drive ordering.

Broader Impacts and Workforce Development

Unique, broad interdisciplinary training will be achieved through Intra- and inter-academic interactions, summer internships at NIST and LANL, participation in synchrotron beamline scattering experiments at AFL and/or being trained on specific theory/modeling at CINT. Materials science and engineering students will be trained to be proficient in computational modeling and ML/AI principles and applications. For student recruitment, we will recruit students from underrepresented groups and from institutions with limited research opportunities. One of the projects impacts stems from the advancement of literacy of AI/ML in materials science. For this, we will exploit the fact that NCSU has a Data Science Academy that offers learning modules and course coordination to students to diffuse best practices in data science and ML/AI. It also offers seed grants to build intellectual and technical data science infra structure – an opportunity the DMREF students should exploit. Georgia Tech has a graduate certificate for Computational Materials Science – courses and certificates the DMREF students will take, including more experimentally trained student

Data Management and Open Access

Our data management plan relies on features and functionality of the Materials Innovation Network/MATIN (https://matin.gatech.edu) at Georgia Tech — a cloud-based e-collaboration platform for accelerating innovation in materials science and engineering (MSE), which is built on the foundation of the opensource software HUBzero (https://hubzero.org). MATIN platform is being funded, developed, and managed by IDEAS:MD3 Center within Georgia Tech's Institute for Materials (IMat).

Advancing Along the Materials Development Continuum and Partnerships to Translation

Advancements in polymer semiconductors are hindered by their complex molecular packing characteristics that drive much of their observed properties. By developing the tools and frameworks to understand the assembly and packing of polymer semiconductors based on their structure will accelerate the advancement of a number of organic electronic technologies such as solar cells and wearable health sensors. The ability to develop this framework required advanced molecular simulations, that then can be used to guide future semiconductor development. The use of ML in phase mapping will accelerate the experimental component of research to ensure we can quickly find meaningful correlations in the vast polymer semiconductors process-structure-property space. We believe that the outcomes will be ML algorithms and MD code that will be adopted by others in the polymer science community. We will make these tools widely available through MATIN as noted above.

Publications and References

Support of this project has resulted in one submitted manuscript and one published paper:
1. M. Wang, X. Xiao, S. Siddika, M. Shamsi, E. Frey, W. Qian, W. Bai, B.T. O'Connor, M.D. Dickey, Glassy gels toughened by solvent. Nature (2024). https://doi.org/10.1038/s41586-024-07564-0.

Discovery of high-strength complex concentrated alloys from physics, machine learning, and experiments

Lead Investigator: Alejandro Strachan. strachan@purdue.edu
Participating Institutions: Purdue University
Source of Support: NSF-DMREF
Website: None.
Keywords: Refractory complex concentrated alloys, CALPHAD, mechanical properties, oxidation resistance.

Project Scope

Refractory complex concentrated alloys (RCCAs) are a new class of materials with an enormous potential for high-temperature structural applications. These alloys exhibit high-temperature strength surpassing Ni superalloys, the current state-of-the-art but their corrosion resistance is far from ideal. We seek to optimize the composition of RCCAs to achieve an unsurpassed combination of strength and oxidation resistance at high temperatures, see Figure 1. This is achieved via a combination of physics-based simulations, multi-resolution experiments, and machine learning. The products of this project will be made available via nanoHUB, where students, educators, and researchers can explore data and perform simulations online.

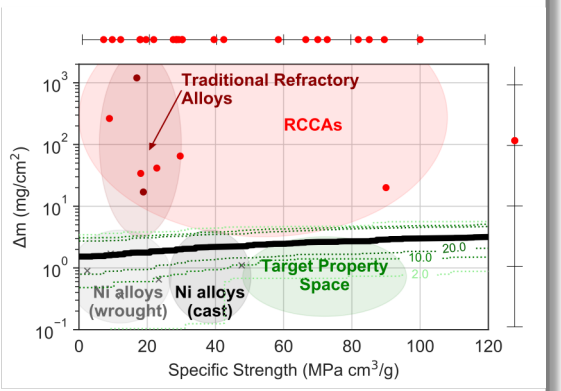


Figure 1. This program seeks to develop RCCAs with an unprecedented combination of strength and oxidation resistance.

Relevance to MGI

The optimization of RCCAs is notoriously difficult due to the high dimensionality of the design space. This project demonstrated that a combination of physics-based modeling, FAIR data, machine learning, experimental fabrication, and multi-resolution characterization can accelerate the design of improved properties. For example, we discovered the hardest Al-containing RCCA with only 24 experiments within a design space consisting of 67,536 possible candidates. Physics-based modeling using CALPHAD reduced the design space by one order of magnitude and a sequential optimization approach based on active learning optimally searched the remaining alloys. A similar strategy is being employed to optimize oxidation resistance. The team started by searching and re-analyzing results from the literature. Results from over 400 alloys were collected analyzed using Bayesian model calibration and made available in a FAIR repository. This exercise enabled our team to start the active learning optimization from a good predictive model. The approach can be generalized to other alloys, and the resulting materials are of interest in applications ranging from aerospace to energy.

Technical Progress

State-of-the-art alloys are engineered to harness strengthening mechanisms across scales, from crystal-level processes to complex hierarchical microstructures designed to hinder the mobility of dislocations and other carriers of plasticity. In this context, complex concentrated alloys (CCAs) are attractive since they can exhibit very high strength at the single-phase level, which can be further enhanced via incorporation of second phaes and microstructural optimization. We demonstrated that a combination of physics-based modeling, machine learning, experimental fabrication, and multi-resolution characterization results in the discovery of the hardest Al-containing BCC-based alloy, surpassing the current state of the art by 41\%. Importantly, this is accomplished with only 24 experiments within a design space consisting of 67,536 possible candidates.
Oxidation modeling is critical to achieving our goal of improving the oxidation resistance of RCCAs. Accomplishments include i) the development of a FAIR database and analysis tools for oxidation mass uptake data to enable data-driven approaches, ii) The tool performs model calibration and selection using Bayesian statistics

and includes a noise parameter to the model to account for the experimental uncertainties and the uncertainties from the data extraction process. and ii) a modified Pilling-Bedworth ratio (PBR) model to better characterize oxide layering in metal alloys. The data and models are being used in our active learning materials discovery effort, described in Section B.

Future Plans

This effort is finishing but the PIs are building on the lessons learned, tools, and data for future efforts.

Broader Impacts and Workforce Development

This project has partially supported six graduate students, one postdoctoral scholar, and four undergraduate students. These researchers are being trained in a multidisplinary environment. The entire DMREF team meets every two weeks and students present their progress and learn about work in other groups. Every student is exposed to and practices the ideas behind MGI. Experimentalists and theoreticians are working together and learning about the details of each other's work.

In collaboration with NSF's Network for Computational Nanotechnology (Strachan is co-PI of NCN), Strachan is a co-organizer of a series of hands-on workshop on machine learning applied to science and engineering problems. Leading experts from around the country make their tools available for online simulations in NSF's nanoHUB and provide a tutorial. Participants can follow the tutorial and perform their own simulations using nanoHUB's cloud resources. The workshops are offered live and are recorded for asynchronous consumption. Interest in the series has been high with 60 to 200 participants in the synchronous sessions. The recorded material and future workshop information can be found at: https://nanohub.org/groups/ml/handsontraining/.

Data Management and Open Access

The following simulation and data resources have been published on nanoHUB.

- Refractory Oxidation Database (https://nanohub.org/tools/refoxdb). Impact: 36 users and data for 405 oxides uploaded. The associated dataset can be found here via the following DOI: doi: 10.21981/30YF-CG46
- Pilling-Bedworth ratio calculator (https://nanohub.org/resources/pbratio). Impact: 219 users.
- PyOxidation (https://nanohub.org/tools/pyoxidation). Impact 32 users.
- Citrine Tools for Materials Informatics (https://nanohub.org/tools/citrinetools). Impact: 646 online simulation users.
- Querying Data Repositories (https://nanohub.org/tools/matdatarepo). Impact: 1235 online simulation users.
- High-Temperature Oxide Property Explorer (https://nanohub.org/resources/htoxideprop). Impact: 87 online simulation users.
- MD sandbox (https://nanohub.org/resources/mdsandbox). Impact 46 online simulation users.
- Active learning challenge for optimal material properties (https://nanohub.org/tools/activelearning). Impact online simulation 60 users.
- Refractory alloys arc melting fabrication (https://nanohub.org/tools/refarcmeltfab). Impact 18 online simulation users.

Advancing Along the Materials Development Continuum and Partnerships to Translation

All the data and tools developed by this effort have been published on nanoHUB and are available for online simulations. We believe that making tools and data FAIR and easily accessible is critical to transfer the technology to students and instructors as well as other researchers in industry, national labs, and academia. The usage numbers of the deployed tools exemplify the impact of this effort.

Publications and References

1. S. Mishra, A. Strachan A. Preferential composition during nucleation and growth in multi-principal element alloys. Journal of Applied Physics. May 14;135 (2024). https://doi.org/10.1063/5.0181330

2. S. Mishra, S. Karumuri, V. Mika V, C. Scott, C. Choy, K. H. Sandhage, I. Bilionis, M. S. Titus, A. Strachan. Mass uptake during oxidation of metallic alloys: Literature data collection, analysis, and FAIR sharing. Computational Materials Science. Jan 30;233:112671 (2024). https://doi.org/10.1016/j.commatsci.2023.112671

3. M.S. Farnell, Z.D. McClure, S. Tripathi, A. Strachan. Modeling environment-dependent atomic-level properties in complex-concentrated alloys. The Journal of Chemical Physics. Mar 21;156 (2022). https://doi.org/10.1063/5.0076584.

4. Z. D. McClure, A. Strachan. Expanding materials selection via transfer learning for high-temperature oxide selection. JOM. Jan;73(1):103-15 (2021). https://doi.org/10.1007/s11837-020-04411-1.

5. D.E. Farache, J.C. Verduzco, Z. D. McClure, S. Desai, A. Strachan. Active learning and molecular dynamics simulations to find high melting temperature alloys. Computational Materials Science. Jun 15;209:111386 (2022). https://doi.org/10.1016/j.commatsci.2022.111386.

Rational design of redox-responsive materials for critical element separations

Lead Investigator: Prof. Xiao Su, x2su@illinois.edu
Participating Institutions: University of Illinois Urbana-Champaign, University of Minnesota
Source of Support: NSF DMREF-2323988
Website: https://dmrefseparation.web.illinois.edu
Keywords: rare-Earth metals, platinum-group metals, electroseparations, redox-polymers, speciation, polymer processing.

Project Scope: The project focuses on designing redox-active polymers for efficiently recovering rare-Earth (REE) and platinum-group (PGM) elements from industrial waste through electroseparations. Creating targeted electrosorbent materials with high selectivity will lead to new classes of separation processes with low waste, high energy efficiency, and integratable with renewable electricity. We are leveraging first-principles electronic structure calculations, operando spectroscopy, force field development, molecular simulations, and machine learning (ML) to guide polymer synthesis for tailored electrochemical binding and good processability. We hypothesize that integrating computational design, characterization of molecular interactions, and rheology will thus accelerate discovery of new redox-sorbents.

Relevance to MGI: The proposed project is closely aligned with the 2021 MGI strategic plan, by bringing a tight integration of experiment, computation, and theory in a framework that is iterative and provides mutual feedback. Unlike earlier trial-and-error approaches, here ML trained on molecular dynamics (MD) and experimental data will guide chemical selection, synthesis, and electrode ink creation to produce ion-selective yet processable redox-polymers to address critical element mixtures of direct relevance to mining and critical materials recycling. Central to our approach is a closed-loop design of molecular binding and polymer secondary structure to accelerate downstream deployment of advanced redox-materials. MD- and electronic structure-guided selection of redox-units, polymer backbones, and solvents that maximize ink stability, paired with advanced rheology and coating processes, will enable creation of electrosorbents with desired macroscopic properties through scaleup, overcoming solubility and processing challenges typical of redox-polymers. Also aligned with goals from the Materials Genome Initiative (MGI), UIUC and UMN will coordinate education and outreach activities aimed at creating a workforce with key competency in data, computation, and experiments.

Technical Progress: PGM and REE recovery have been pursued in parallel. For PGMs, **Su** synthesized redox-metallopolymers with tunable redox-potentials and demonstrated molecular selectivity in multicomponent PGM mixtures.[1] Versus standard electrosorption, iridium recovery required 75% less energy. Using a redox-polymer electrosorbent, >186 mmol Pd/mol ferrocene was achieved in a real-world catalytic converter leach solution (**Figure 1**). Redox-electrosorbents were translated onto continuous redox-extraction using hydrophobic functionalization of ferrocenes.[2] Continuous electrified liquid-liquid extraction was deployed to selectively recover dilute gold and PGMs – demonstrating exceptional atomic efficiency (>90%), >100:1 selectivity, and 16-fold up-concentration in contaminated metal leaches. For REEs, **Shukla** leverages ML to create new ligands for **Su** to synthesize and test. **Shukla** and **Su** are categorizing data for REEs and ligand affinity, by collating datasets of >7000 literature thermodynamic data points from >700 unique ligands with REEs. A pre-trained chemical language model was created to aid materials discovery. Simultaneously, **Su** is establishing fast-throughput screening for benchmarking ligand affinity via solvent-extraction. **Jain** uses Raman scattering spectroscopy to reveal unknown speciations of REE and PGM complexes, characterize structures, and probe electrosorption. Ferricyanide and ferrocyanide complexes with well-known structures were the model solution-phase Raman spectra used to benchmark density functional theory (DFT); bond lengths and Raman mode frequencies were predicted within 2-4% of experiments. We are now using Raman scattering spectroscopy and

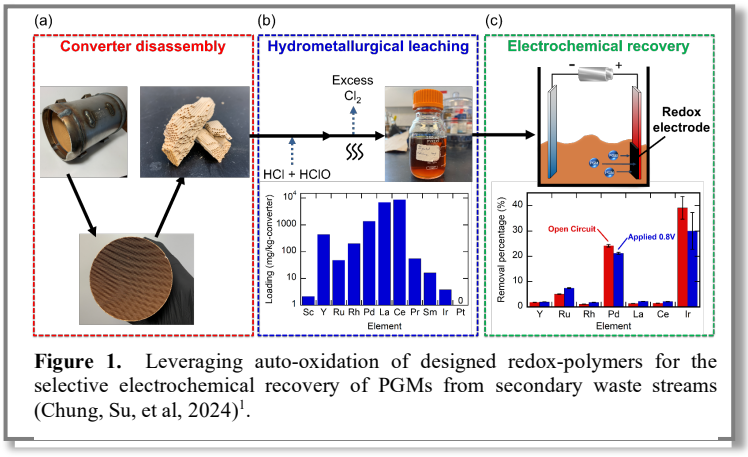


Figure 1. Leveraging auto-oxidation of designed redox-polymers for the selective electrochemical recovery of PGMs from secondary waste streams (Chung, Su, et al, 2024)[1].

DFT to characterize yttrium and samarium hydrates. Newly-identified speciations and REE complex structures will be added to the materials data repository. **Calabrese** has developed and processed electrode inks (redox-active polymer/carbon nanotubes/solvent). To overcome previous measurement challenges (ink volatility, large sample volume), a custom dripping-onto-substrate device was used. Measurements on moderate molecular weight inks revealed low-elasticity and good processability. To improve processability of higher-MW polymers, we combined co-solvents with a high-MW polymer used by **Su**, revealing a promising route for incorporating high-MW polymers into electrodes. Long MD simulations (**Shukla**) require accurate and inexpensive force fields– largely missing for REEs and PGMs. Here, **Mironenko** is generalizing non-empirical tight binding theory[3] to describe non-bonded interactions between REEs with water and redox-active materials. Our work improves upon currently available force-fields[4] which fail to capture necessary physics, including inter-molecular charge transfer. Our results for [La^{3+}-H_2O] demonstrate an excellent match between contributions obtained from ALMO-EDA energy decomposition analysis and simple, analytical, and physics-inspired functional forms.

Future Plans: The current goals from the **Su group** is unraveling the fundamental systematic principles for PGM and REE binding under electric fields and redox-reactions. The students will be working closely with the **Jain** and **Mironenko** group to leverage spectroscopy and electronic structure calculations as design tools for identifying major binding motifs, as well as carrying out new synthetic modifications. Alongside the **Calabrese group**, we will be adjusting our polymer structures for improved coatability, and finally, we will finalize establishing high-throughput testing methods for REEs to carry out the next stage screening for the ML-methods developed by the **Shukla** group. Immediate future goals in the **Calabrese** lab are to submit the publication on using cosolvents to improve polymer processability. Ongoing work with the **Su** group extends the previous studies on poly(ferrocenyl methyl methacrylate) to PGM capture. We are examining extensibility as a function of molecular weight and cosolvent content and working on controlled production of polymers with lower polydispersity, greater processability, and extensional flow behavior. In the **Mironenko** group, we are extending the current force field model for [La^{3+}-H_2O] to improve electrostatics and charge-transfer and account for modulations of functional forms and parameters by the La^{3+}-H_2O coordination. Using *ab initio* thermodynamics, free energy minimizing ligand-metal combinations will also be studied to guide design of ligands with improved binding and stability. Ultimately, large-scale screening data will be generated to parameterize ML for predicting new redox groups beyond the existing library to be incorporated into synthesized polymers (**Su, Calabrese**), forming a closed loop, computationally-guided approach to polymer development.

Broader Impacts and Workforce Development: This project will help establish a US supply chain for REEs and PGMs used in many electronics and clean technologies, which is critical for US national security and economic prosperity. The integrated computational/experimental approach will advance ML fundamentals and materials design, and can be generalized for materials for water purification, energy storage, and electrocatalysis. In July 2024, **Su**, **Shukla**, **Jain**, and **Mironenko** organize a camp for the Worldwide Youth in Science and Engineering (WYSE) program and a Women Focused Summer camp, Catalyzing UR Interest in Engineering (CURIE) in collaboration with Society of Women Engineers and College of Engineering at UIUC. **Shukla** directs this week-long camp, which hosts 30 female high schoolers interested in pursuing chemical engineering in college. As part the lab activities, **Su** and **Jain** will organize a hands-on demonstration focused on water purification to simulate REE removal. **Shukla** and **Mironenko** will organize a computational activity focused on introducing structure–function relationship for materials used for ion separations, using data generated in the proposed research.

Data Management and Open Access: The data will be available for access in accordance with FAIR Guiding Principles for scientific data management and stewardship. Manuscripts and supporting information resulting from work supported by this grant will be posted on the NSF Public Access Repository. When larger datasets are developed that span multiple publications, data will be stored at the data repository of the University of Minnesota (DRUM) and Illinois Data Bank which provides automatic digital object identifiers (DOIs) for easy access by the public. Rich metadata will be included with all the experimental and computational datasets to improve reusability and interoperability.

Advancing Along the Materials Development Continuum and Partnerships to Translation: The key to accelerating design and processability of redox-active materials for electroseparations is the integrated computational/experimental approach, which can be generalized for materials for water purification, energy storage, and electrocatalysis. Pathways for scaling up electrode production will also contribute towards manufacturing and translation of this technology. The computer packages, methods, and databases generated will be made publicly available and can be translated and adopted for different material classes and electroseparation systems within the community.

Publications and References:

1. C.-H. Chung, S. Cotty, J. Jeon, J. Elbert, X. Su. *Auto-oxidation of redox electrodes for the selective recovery of platinum group metals.* Journal of Materials Chemistry A **12**, 15006-15018 (2024). DOI: 10.1039/D4TA01384K.
2. S. R. Cotty, A. Faniyan, J. Elbert, and X. Su. *Redox-mediated electrochemical liquid–liquid extraction for selective metal recovery.* Nature Chemical Engineering **1**, 281-292 (2024). DOI: 10.1038/s44286-024-00049-x.
3. A. V. Mironenko. *Analytical and Parameter-Free Huckel Theory Made Possible for Symmetric H(x) Clusters.* The Journal of Physical Chemistry A **127**, 7836-7843 (2023). DOI: 10.1021/acs.jpca.3c03646.
4. E. E. Wait, J. Gourary, C. Liu, E. D. Spoerke, S. B. Rempe, P. Ren. *Development of AMOEBA Polarizable Force Field for Rare-Earth La3+ Interaction with Bioinspired Ligands.* The Journal of Physical Chemistry B **127**, 1367-1375 (2023). DOI: 10.1021/acs.jpcb.2c07237.

BEAST DB: Grand-Canonical Database of Electrocatalyst Properties

Lead Investigator: Ravishankar Sundararaman, sundar@rpi.edu
Participating Institutions: Rensselaer Polytechnic Institute; University of Colorado Boulder; National Renewable Energy Laboratory; University of South Carolina; Lawrence Berkeley National Laboratory
Source of Support: DOE-BES (award ID: DE-SC0022247)
Website: Information on codes, publications and workshops by the BEAST team are up to date on https://beast-echem.org, which serves as a continuing central repository for disseminating all results of this program. We have also publicly released the BEAST DB at https://beastdb.nrel.gov, linked prominently from our main project website.
Keywords: Computational electrocatalysts, Solvation, Beyond-DFT, Machine learning,

Project Scope: The BEAST project aims to deliver exascale-ready solvated beyond-DFT methods and machine learning (ML) acceleration using an electrochemical database to make truly ab initio electrochemistry accessible and ubiquitous. This project aims to address the two key challenges in theoretical understanding of electrochemical reactions: (1) the lack of a universal framework that efficiently treats arbitrary electrolytes, solvents and applied potentials with sufficient detail and fidelity to realistically and accurately model electrochemical systems, and (2) the deficiencies of density functional theory (DFT) in describing charge transfer and reaction barriers.

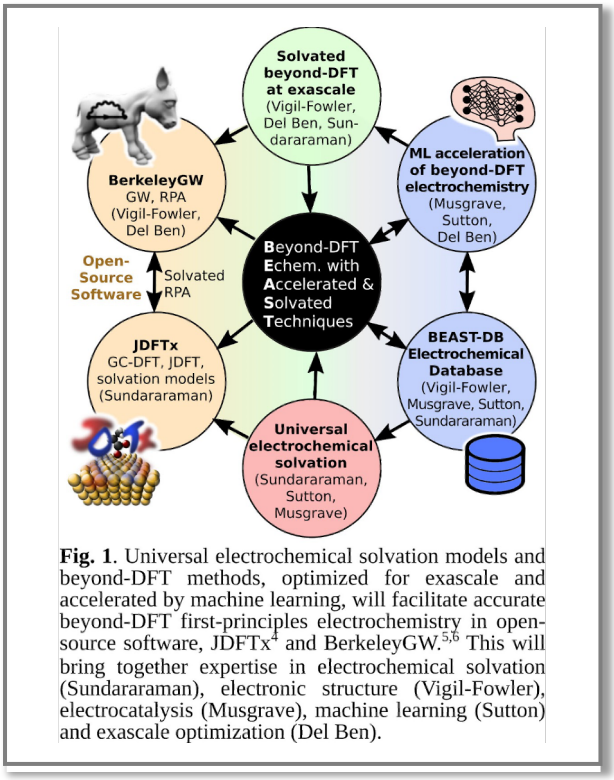


Fig. 1. Universal electrochemical solvation models and beyond-DFT methods, optimized for exascale and accelerated by machine learning, will facilitate accurate beyond-DFT first-principles electrochemistry in open-source software, JDFTx[4] and BerkeleyGW.[5,6] This will bring together expertise in electrochemical solvation (Sundararaman), electronic structure (Vigil-Fowler), electrocatalysis (Musgrave), machine learning (Sutton) and exascale optimization (Del Ben).

Relevance to MGI: Although our collaboration does not involve a synthetic effort, researchers can query BeastDB to find materials with specific properties, thereby guiding the experimental dentification of new catalysts and potentially reducing the development cycle. Moreover, one of the significant advancements facilitated by BeastDB is the ability to train machine learning models that can predict material properties without relying on DFT. This capability not only accelerates the discovery and development of new materials but also democratizes access to high-level predictive tools, enabling a broader range of researchers to contribute to the field.

Technical Progress:

- ***BEAST DB grand-canonical electrocatalysis database:*** We publicly released BEAST DB (https://beastdb.nrel.gov, *arXiv:***2405**.20239), which allows for searches by reactions and adsorbates, sortable by reaction activity descriptors (Figure 1). The BEAST DB contains over 21,000 surface calculations that span four material spaces and four electrochemical reactions. It provides standard catalysis models (4 layer stepped and flat metal surfaces) usable as a baseline for comparison, as well as binary covalent alloys, bimetallic single atom alloys, and single atom nitrogen doped graphene 2D catalysts. The exotic material spaces can break traditional catalytic scaling relations, and serve as a jumping-off point for finding more active electrocatalysts.

- ***Beyond-DFT solvated methods at exascale:*** Regarding our work on solvation, to enable an analogous first-principles approach towards classical DFT solvation, we have developed techniques to train MLIPs that are better suited for the modeling of inhomogeneous liquids (JCC 2024, 1, DOI: 10.1002/jcc.27353). Furthermore, we have successfully developed a universal neural network framework for learning nonlocal DFT functionals in 1D for both *classical* (liquid) and *quantum* (electronic) systems. By combining equivariant neural networks with the weighted density approximation from classical DFT, our method learns near-exact DFT functionals for the 1D hard-rod fluid, the Ising model, Hartree-Fock exchange, the Kohn-Sham kinetic energy and liquid water all while using the *same hyperparameters and training protocols* (arXiv:**2405**.20270 (2024)).

  We have also worked on Beyond-DFT solvation GW by interfacing JDFTx and BerkeleyGW (J. Appl. Phys. 134, 085001 (2023)). The developed interface between JDFTx-BerkeleyGW allows dense diagonalization of GW/RPA calculations in JDFTx. For example, we completed a simulation containing 265 atoms, 1744 electrons and 150,000 bands (an O_2 on 4x4 Pt surface with water and a nafion fragment) in less than a day on 1040 cores on NREL's Kestrel supercomputer.

  Through this collaboration, significant progress has been made towards s*calable GW/RPA calculations of metal surfaces* for beyond-DFT electrochemistry (*arXiv:*2405.20258 (2024)). As a result, we have identified a recommended workflow for accurate RPA total energies of larger systems, scalable to exascale machines and at reduced cost enabling beyond-DFT simulations of molecules, surfaces and bulk systems (*chemrxiv*-**2024**-25pch). For example, we ran RPA for the 4x4 Pt+O_2+water+Nafion system on 64 Kestrel H100 GPUs, and calculated the full ORR pathway using both DFT and RPA on a 2x2 Pt surface. Most impressively, this implementation tested for BEAST-relevant catalytic Pt surfaces shows an effective $O(N^2)$ scaling (Figure 2), and has been made publicly available within BerkeleyGW 4.0.

- ***Machine-learned acceleration of BEAST-DB***. We adapted the state-of-the-art architecture Atomistic Line Graph Neural Network (ALIGNN), to encode PBE eigenvalues and bias voltage as global features and orbital projections as node-level features, which achieved 0.10 eV accuracy, enabling HSE06-level accuracy at PBE-level cost for catalysts. We are also developing a generalized BEAST MLIP) trained to representative calculations in BEAST DB that approaches DFT accuracy at orders of magnitude lower cost. We have tested our new MLIP on HER, OER, ORR and NRR pathways, and are testing its potential for out-of-box screening of reaction pathways on unseen catalysts, including reaction barriers from ML-optimized transition states.

Future Plans: Expand BEAST DB with community input, targeting the most promising catalysts for various chemistries and including complexities in the catalyst representation that have not been included to date, e.g. surface coverage, defects; Perform solvated fixed-potential surface Pourbaix analysis on the metal catalysts in the dataset to estimate surface coverages at a range of operating conditions; Benchmark RPA forces algorithms employing a hybrid approach between JDFTx/QimPy and BerkeleyGW. Identify methodology and challenges in implementing solvated RPA Improved electronic functionals for beyond-semilocal DFT; Extend the equivariant ML-DFT framework to 3D, and test classical DFTs for solvation in DFT calculations in QimPy; Develop a simplified implicit solvation model incorporating molecular dynamics response results for more rapid electrochemical solvation than a full classical DFT approach.

Broader Impacts and Workforce Development: Beyond offering numerous opportunities for training and professional development of the postdocs and graduate students within the project, for the past two years, our project has conducted a BEAST workshop (online in 2022, and in a hybrid format in 2023 at

Cal State University in Oakland, CA). Last year the in-person attendance of 20 early-career researchers in Oakland, CA with over 50 virtual attendees additionally. A similar in-person/hybrid workshop is being held at University of Colorado, Boulder immediately following the ACS Fall meeting on August 22-23, 2022. The workshop covers the current state-of-the-art first-principles electrochemical simulations using JDFTx and solvated GW/RPA using BerkeleyGW starting from JDFTx, as well as introduce preliminary capabilities of the QimPy code and machine learning. Moreover, under the auspicious of the BEAST, project, co-PI Sutton organized a five-day tutorial on machine learning for the graduate students in the UTEP Physics Dept. in April 2024.

Data Management and Open Access

We have numerous open-source software contributions:

- *Ab initio* molecular dynamics in external potentials for training neural network potentials of inhomogeneous fluids implemented within JDFTx (https://jdftx.org). Implemented the calculation and output of the rALDA kernel for use in BerkeleyGW.
- JDFTx electronic structure processing to easily visualize DOS and COHP (https://github.com/benrich37/ultraSoftCrawfish)
- New framework using LAMMPS to test inhomogeneous fluid response using classical and neural network potentials, MDext (https://github.com/shankar1729/mdext)
- Frameworks for machine learned functionals, molecular dynamics and solvation implemented into QimPy (https://qimpy.org), the JDFTx successor that will host the unified electrochemical software capabilities of the BEAST project by its end
- The GPU offload Full-Frequency GW and RPA within the static subspace formalism and NV-Block implementation including support for partial occupations has been released into the public release of BerkeleyGW, as has the solvated GW code.
- We have also publicly released the BEAST DB at https://beastdb.nrel.gov, with a highly responsive user interface and MongoDB backend scalable for continuing expansion of our dataset. The frontend allows searching by reactions and adsorbates, sortable by reaction activity descriptors, enabled by a React application that builds each page dynamically and asynchronously (AJAX).

Advancing Along the Materials Development Continuum and Partnerships to Translation: To facilitate the discovery of new electrocatalyst, accurate and reliable computational methods are needed to gain a deeper understanding of the complex structure property relationships in these systems. Through the BEAST project we have develop several new approaches and methods – all of which are open source -- as well as an extensive public database of over 20,000 surface calculations Grand-Canonical DFT calculations to accelerate the materials discovery process. Although BEASTDB is focused on discovery and design of new electrocatalyst, the fundamental software capabilities for solvated electronic structure calculations can potentially extend far beyond electrocatalysis to include diverse fields spanning biochemistry to quantum materials. The code capabilities within JDFTx, QimPy and BerkeleyGW added by this project, such as high-efficiency DFT on GPUs and cubic-scaling RPA, will be useful beyond our project.

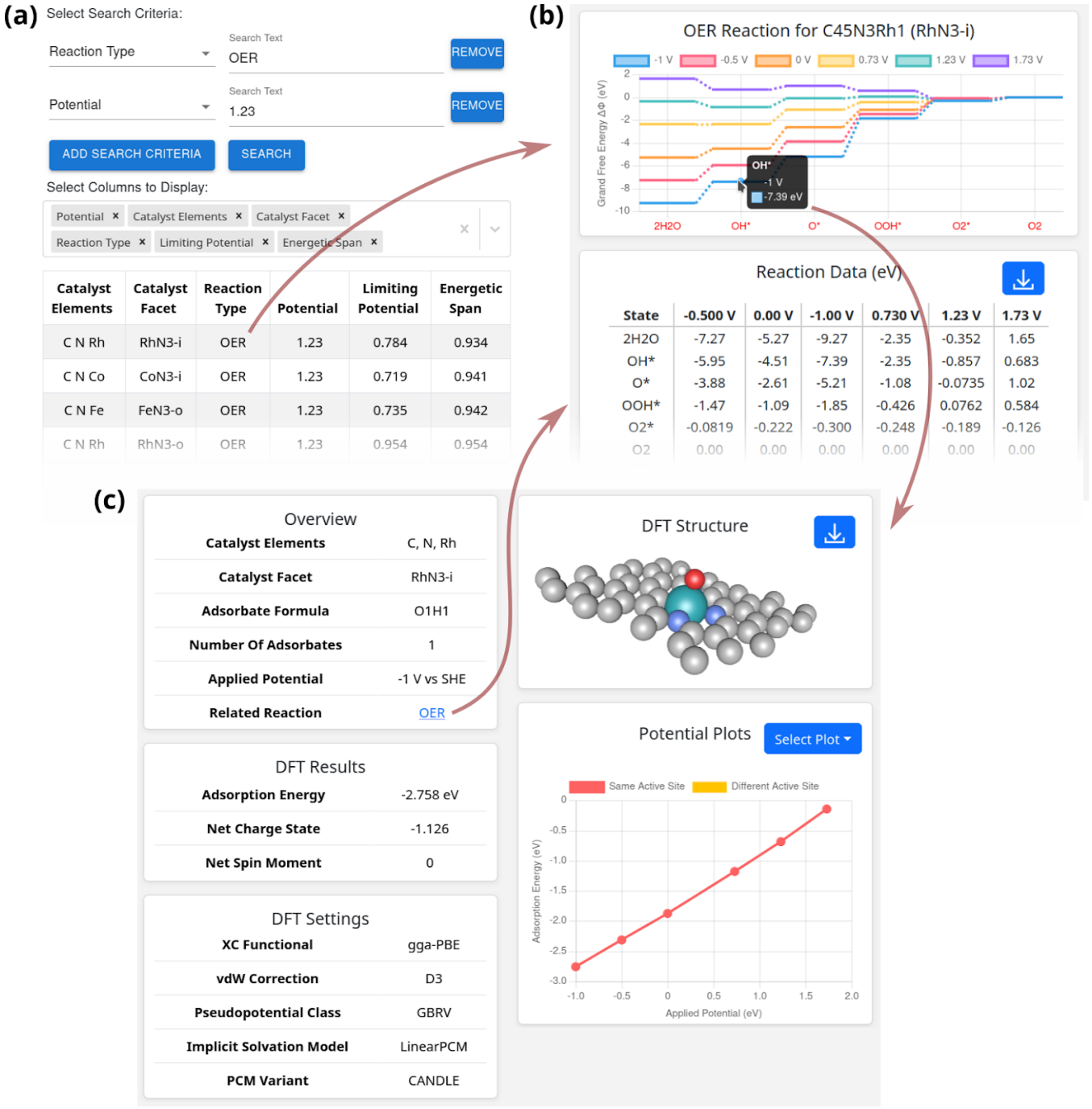


Figure 1. BEAST-DB user interface. (a) Reaction search based on catalyst elements, reaction type, potential and activity descriptors, shown here for OER at 1.23 V with sorting based on the energetic span. Each row links to (b) a detailed view of the reaction pathway as a function of potential. Each intermediate in the pathways links to (c) a detailed view of a specific catalyst with adsorbate calculation, including calculation details and plots of the structure and potential dependence of properties such as energy and charge (selectable). BEAST DB also allows searching directly for the adsorbates on catalysts (not shown here), linking to (c), which in turn links to corresponding reaction pathways.

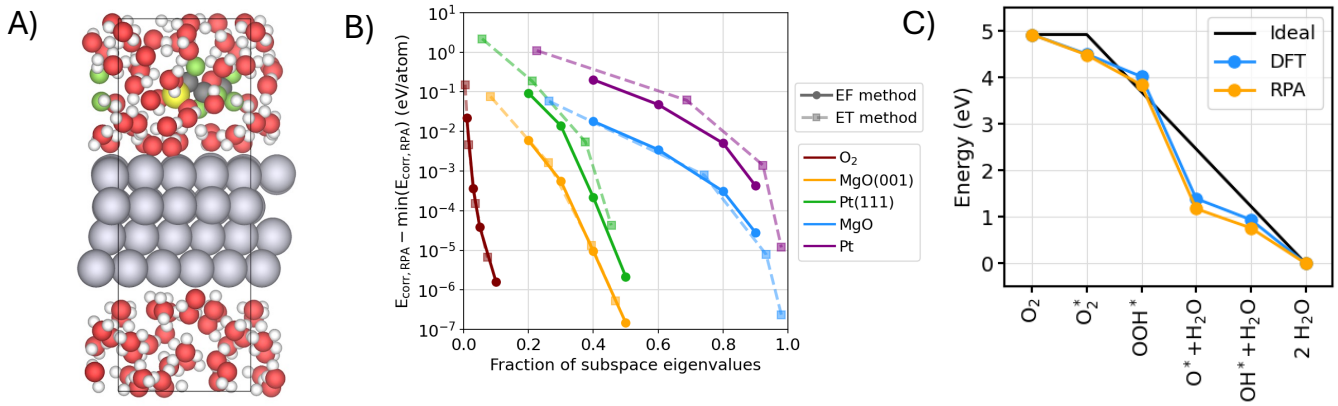


Figure 2. **A)** 4x4 Pt surface + O_2 + explicit water + Nafion fragment + hydronium system used for the solvated RPA calculation. **B)** Error to the RPA correlation energy introduced by using the subspace approximation. This error is controlled by an input file parameter that determines how many subspace eigenvalues and eigenvectors of the entire basis set are retained in the calculation, with more resulting in better accuracy and higher cost. The error is highly dependent on the dimensionality of the system, with calculations for molecules (here, only O_2 is shown) and quasi-2D surfaces (here, only MgO(001) and Pt(111) are shown) requiring less the 5 and 40%, respectively, of the basis set for 10^{-3} eV/atom accuracy in the RPA correlation energy as compared to using more eigenvalues/vectors. The method used to select eigenvalues/vectors for truncation also matters (dashed vs solid lines), with the method dependent on the dielectric matrix head (the ET method) converging worse for metallic systems. **C)** DFT and RPA energies for the oxygen reduction reaction pathway on 2x2 Pt(111) assuming the associative mechanism. The RPA energies are stabilized as compared to DFT for the OOH, O, and OH states.

Publications and References

1. C. Tezak, J. Clary, S. Gerits, J. Quinton, B. Rich, N. Singstock, A. Alherz, T. Aubry, S. Clark, R. Hurst, M. Del Ben, C. Sutton, R. Sundararaman, C. Musgrave and D. Vigil-Fowler, "BEAST DB: Grand-Canonical Database of Electrocatalyst Properties", arXiv:2405.20239 (2024)

2. D. Weinberg, O. A. Hull, J. M. Clary, R. Sundararaman, D. Vigil-Fowler and M. Del Ben, "Static Subspace Approximation for Random Phase Approximation Correlation Energies: Implementation and Performance", arXiv:2405.20258 (2024)

3. J. M. Clary, O. A. Hull, D. Weinberg, R. Sundararaman, M. Del Ben and D. Vigil-Fowler, "Static Subspace Approximation for Random Phase Approximation Correlation Energies: Applications to Materials for Catalysis and Electrochemistry", chemrxiv-2024-25pch (2024)

4. M. M. Kelley, J. Quinton, K. Fazel, N. Karimitari, C. Sutton and R. Sundararaman, "Bridging electronic and classical density-functional theory using universal machine-learned functional approximations", arXiv:2405.20270 (2024)

5. K. Fazel, N. Karimitari, T. Shah, C. Sutton and R. Sundararaman, "Improving the reliability of machine learned potentials for modeling inhomogeneous liquids", J. Comput. Chem. 45, 1821 (2024)

6. J Clary, M Del Ben, R Sundararaman, D Vigil-Fowler, "Impact of solvation on the GW quasiparticle spectra of molecules", J. Appl. Phys. 134, 085001 (2023)

7. S Adhikari, J Clary, R Sundararaman, C Musgrave, D Vigil-Fowler, C Sutton, "Accurate Prediction of HSE06 Band Structures for a Diverse Set of Materials Using Δ-Learning", Chem. Mater. 35, 8397–8405 (2023)

8. C. Tezak, N. Singstock, A. AlHerz, D. Vigil-Fowler, C. Sutton, R. Sundararaman and C. Musgrave, “Revised Nitrogen Reduction Scaling Relations from Potential-Dependent Modeling of Chemical and Electrochemical Steps”, ACS Catal. 13, 12894–12903 (2023)

9. M. Woodcox, A. Mahata, A. Hagerstrom, A. Stelson, C. Muzny, R. Sundararaman and K. Schwarz, “Simulating dielectric spectra: A demonstration of the direct electric field method and a new model for the nonlinear dielectric response”, J. Chem. Phys. 158, 124122 (2023)

10. R. Sundararaman and K. Schwarz, “Solvent effects determine the sign of the charges of maximum entropy and capacitance at silver electrodes”, J. Chem. Phys. 158, 121102 (2023)

11. N. R. Singstock, C. B. Musgrave, “How the Bio-Inspired Fe2Mo6S8 Chevrel Breaks Electrocatalytic Nitrogen Reduction Scaling Relations”, J. Am. Chem. Soc. 144, 28 (2022)

12. R. Sundararaman, D. Vigil-Fowler and K. Schwarz, “Improving the Accuracy of Atomistic Simulations of the Electrochemical Interface”, Chem. Rev. 122, 10651 (2022)

13. Shandilya, K. Schwarz and R. Sundararaman, “Interfacial water asymmetry at ideal electrochemical interfaces”, J. Chem. Phys. 156, 014705 (2022)

14. Y. A. Alsunni, A. W. Alherz, and C. B. Musgrave, “Electrocatalytic Reduction of CO2 to CO over Ag(110) and Cu(211) Modeled by Grand-Canonical Density Functional Theory”, J. Phys. Chem. C 125, 23773 (2021)

SPARC-X: Quantum simulations at extreme scale – reactive dynamics from first principles

Lead Investigator: Phanish Suryanarayana, phanish.suryanarayana@ce.gatech.edu
Participating Institutions: Georgia Institute of Technology, Lawrence Livermore National Laboratory
Source of Support: DOE-BES: DE-SC0019410, DE-SC0023445
Website: https://github.com/SPARC-X
Keywords: Kohn-Sham, Density functional theory, Electronic structure, Real-space, Software

Project Scope

The objective of this project is to develop SPARC-X: an open source computational framework for performing Kohn-Sham Density Functional Theory (DFT) calculations, including those that scale linearly with system size, which can leverage petascale/exascale parallel computers to study chemical phenomena at length and time scales previously accessible only by empirical approaches — e.g., 100,000 atoms for a few picoseconds using semilocal functionals, 1000 atoms for a few nanoseconds using hybrid functionals, or 1000 atoms for a few picoseconds at the level of random phase approximation (RPA) correlation energy. SPARC-X will be augmented with the capability to perform on-the-fly machine-learned force field (MLFF) simulations with Δ-machine learning, where recent breakthroughs in fingerprinting schemes and Gaussian process regression (GPR) approaches will push the boundaries of chemical complexity and system size that can be studied using such methods, enabling time scales that are a further two orders of magnitude larger.

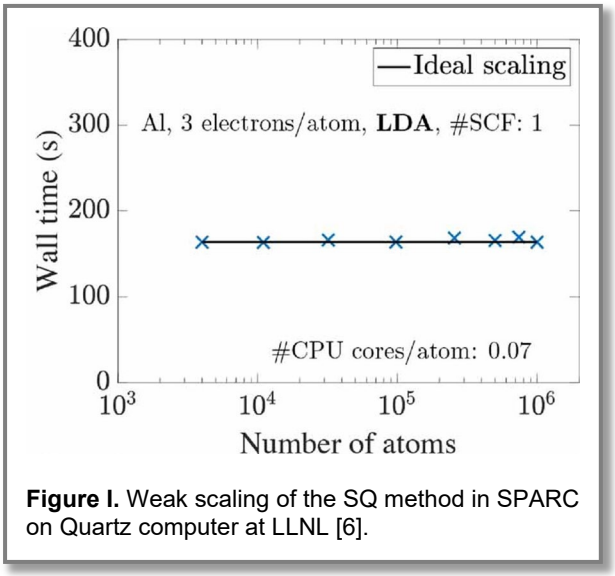


Figure I. Weak scaling of the SQ method in SPARC on Quartz computer at LLNL [6].

Relevance to MGI

Over the course of the past few decades, quantum mechanical calculations based on Kohn–Sham DFT have become a cornerstone of materials research by virtue of the predictive power and fundamental insights they provide. The tremendous popularity of DFT can be attributed to its generality, simplicity, and highly favorable accuracy-to-cost ratio relative to other such ab initio theories. However, Kohn-Sham calculations are associated with large computational expense, which severely limits the range and type of physical systems that can be investigated. In particular, the computational design process for materials is severely restricted by the large time to solution associated with such simulations. The objective of this project is to develop a computational framework that accelerates Kohn-Sham DFT calculations by orders of magnitude (Fig. I), which would make it an attractive choice for use in frameworks targeted towards the design of new materials with tailored properties.

Technical Progress

In this project, an open-source, real-space density functional theory (DFT) code named SPARC [4, 16] has been developed. It accommodates both Dirichlet and Bloch-periodic boundary conditions, enabling the treatment of finite, semi-infinite, and charged systems, as well as bulk 3D systems. Current features of SPARC include: (i) applicable to isolated systems such as molecules as well as extended systems such as crystals, surfaces, and wires [16]; (ii) local, semilocal, and hybrid exchange-correlation functionals [1, 4, 16]; (iii) dispersion interactions through DFT-D3, vdW-DF1, and vdW-DF2 [4]; (iv) norm conserving pseudopotentials, including nonlinear core corrections [12]; (v) spin polarized and unpolarized calculations [4, 16]; (vi) spin-orbit coupling [4]; (vii) calculation

of ground state energy, atomic forces, and stress tensor [4, 16]; (viii) structural relaxation and ab initio molecular dynamics (NVE, NVT, and NPT) [4, 16], (ix) linear-scaling, i.e., O(N), Spectral Quadrature (SQ) method [8]; (x) Discrete Discontinuous Basis Projection (DDBP) method [19]; (xi) MATLAB version available for rapid prototyping: M-SPARC [11, 18]; (xii) spectral scheme for atomic structure calculations [2]; (xiii) on-the-fly MLFFs using smooth overlap of atomic positions (SOAP) and Gaussian multipole (GMP) descriptors [3, 6]; (xiv) self-consistent convolutional density functional approximations [5]; (xv) Δ-machine learning [6]; (xvi) density functional perturbation theory (DFPT) [7]; (xvii) orbital-free DFT [9, 20]; and (xviii) GPU acceleration of local, semilocal, and hybrid exchange-correlation functionals [10].

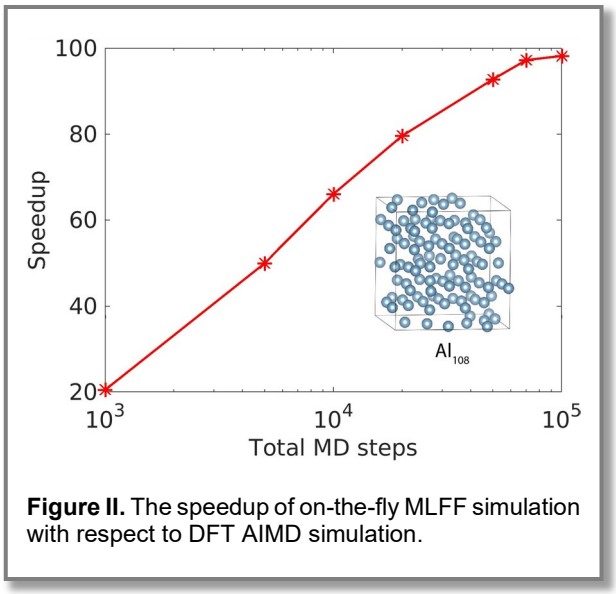


Figure II. The speedup of on-the-fly MLFF simulation with respect to DFT AIMD simulation.

SPARC is not only portable, but is also straightforward to install, use, and modify, with external dependencies limited to industry standard MPI, BLAS, and LAPACK/ScaLAPACK. It has been extensively benchmarked and validated against well established planewave codes, where SPARC has shown to be an order of magnitude faster in time to solution, with increasing advantages as the number of processors is increased. It can efficiently utilize modest as well as large-scale computational resources, with parallel scaling bringing solution times to a few seconds for O(100-500) atoms and about a minute for systems with O(500-1000) atoms. Using the O(N) SQ method, SPARC has been scaled to system sizes containing more than a million atoms (Fig. I). Using the on-the-fly MLFF implementation, the time scales accessible has been increased by two orders-of-magnitude (Fig. II). SPARC is freely available at: https://github.com/SPARC-X/SPARC.

Future Plans

Key developments targeted in SPARC include: (i) GPU acceleration for the calculation of the RPA correlation energy, (ii) GPU acceleration of the on-the-fly MLFFs, (iii) GPU acceleration of DFPT, and (iv) novel formulations for the RPA correlation energy with reduced prefactor.

Broader Impacts and Workforce Development

All codes and data are made freely available at https://github.com/SPARC-X. The project provides a unique opportunity to conduct research and mentor/train postdoctoral scholars as well as graduate students in an area which is at the interface of chemistry, applied mathematics, physics, materials science, and high performance computing.

Data Management and Open Access

All codes and data made freely available at https://github.com/SPARC-X.

Advancing Along the Materials Development Continuum and Partnerships to Translation

No plans for commercialization.

Publications and References

1. X. Xing and P. Suryanarayana, *Efficient real space formalism for hybrid density functionals*, arXiv:2406.16998 (2024). DOI: 10.48550/arXiv.2406.16998
2. S. Bhowmik, J. E. Pask, A, J. Medford, and P. Suryanarayana, *Spectral scheme for atomic structure calculations in density functional theory*, arXiv:2406.00534 (2024). DOI: 10.48550/arXiv.2406.00534

3. L. R. Timmerman, S. Kumar, P. Suryanarayana, and A. J. Medford, *Overcoming the Chemical Complexity Bottleneck in on-the-Fly Machine Learned Molecular Dynamics Simulations*, J. Chem. Theory and Comput.., **20**(14), 5788-5795 (2024). DOI: 10.1021/acs.jctc.4c00474
4. B. Zhang, X. Jing, Q. Xu, S. Kumar, A. Sharma, L. Erlandson, S. J. Sahoo, E. Chow, A. J. Medford, J. E. Pask, and P. Suryanarayana, *SPARC v2.0.0: Spin-orbit coupling, dispersion interactions, and advanced exchange–correlation functionals*, Software Impacts, **20**, 100649 (2024). DOI: 10.1016/j.simpa.2024.100649
5. S. J. Sahoo, Q. Xu, X. Lei, D. Staros, G. R. Iyer, B. Rubenstein, P. Suryanarayana, and A. J. Medford, *Self-Consistent Convolutional Density Functional Approximations: Application to Adsorption at Metal Surfaces*, ChemPhysChem, **25**, e202300688 (2024). DOI: 10.1002/cphc.202300688
6. S. Kumar, X. Jing, J. E. Pask, A. J. Medford, and P. Suryanarayana, *Kohn–Sham accuracy from orbital-free density functional theory via Δ-machine learning*, J. Chem. Phys., **159**, 244106 (2023). DOI: 10.1063/5.0180541
7. A. Sharma and P. Suryanarayana, *Calculation of phonons in real-space density functional theory*, Phys. Rev. E, **108**, 045302 (2023). DOI: 10.1103/PhysRevE.108.045302
8. V. Gavini, S. Baroni, V. Blum, D. R Bowler, A. Buccheri, J. R Chelikowsky, S. Das, W. Dawson, P. Delugas, M. Dogan, C. Draxl, G. Galli, L. Genovese, P. Giannozzi, M. Giantomassi, X. Gonze, M. Govoni, F. Gygi, A. Gulans, J. M. Herbert, S. Kokott, T. D Kühne, K-H Liou, T. Miyazaki, P. Motamarri, A. Nakata, J. E. Pask, C. Plessl, L. E. Ratcliff, R. M. Richard, M. Rossi, R. Schade, M. Scheffler, O. Schütt, P. Suryanarayana, M. Torrent, L. Truflandier, T. L. Windus, Q. Xu, V. W-Z Yu, and D. Perez, *Roadmap on Electronic Structure Codes in the Exascale Era*, Modelling Simul. Mater. Sci. Eng. **31**, 063301 (2022). DOI: 10.1088/1361-651X/acdf06
9. B. Thapa, X. Jing, J. E. Pask, P. Suryanarayana, and I. I. Mazin, *Assessing the source of error in the Thomas–Fermi–von Weizsäcker density functional*, J. Chem. Phys., **158** (21), 214112 (2023). DOI: 10.1063/5.0146167
10. A. Sharma, A. Metere, P. Suryanarayana, L. Erlandson, E. Chow, and J. E. Pask, *GPU acceleration of local and semilocal density functional calculations in the SPARC electronic structure code*, J. Chem. Phys., **158** (20), 204117 (2023). DOI: 10.1063/5.0147249
11. B. Zhang, X. Jing, S, Kumar, and P. Suryanarayana, *Version 2.0.0 - M-SPARC: Matlab-Simulation Package for Ab-initio Real-space Calculations*, SoftwareX, **21**, 101295 (2023). DOI: 10.1016/j.softx.2020.100423
12. Mostafa Faghih Shojaei, John E. Pask, Andrew J. Medford, Phanish Suryanarayana, *Soft and transferable pseudopotentials from multi-objective optimization*, Comput. Phys. Comm., **283**, 108594 (2023). DOI: 10.1016/j.cpc.2022.108594
13. S. Shah, P. Suryanarayana, and E. Chow, *Pseudodiagonalization Method for Accelerating Nonlinear Subspace Diagonalization in Density Functional Theory*, J. Chem. Theory and Comput., **18**, 6, 3474–3482 (2022). DOI: 10.1021/acs.jctc.2c00166
14. Q. Xu, X. Jing, B. Zhang, J. E. Pask, and P. Suryanarayana, *Real-space density kernel method for Kohn–Sham density functional theory calculations at high temperature*, J. Chem. Phys., **156**, 094105 (2022). DOI: 10.1063/5.0082523
15. S. J. Sahoo, X. Jing, P. Suryanarayana, and A. J. Medford, *Ab-Initio Investigation of Finite Size Effects in Rutile Titania Nanoparticles with Semilocal and Nonlocal Density Functionals*, J. Phys. Chem. C, **126**, 4, 2121(2022). DOI: 10.1021/acs.jpcc.1c08915
16. Q. Xu, A. Sharma, B. Comer, H. Huang, E. Chow, A. J. Medford, J. E. Pask, and P. Suryanarayana, *SPARC: Simulation Package for Ab-initio Real-space Calculations*, SoftwareX, **15**, 100709 (2021). DOI: 10.1016/j.softx.2021.100709
17. C. M. Diaz, P. Suryanarayana, Q. Xu, T. Baruah, J. E. Pask, and R. R. Zope, *Implementation of Perdew--Zunger self-interaction correction in real space using Fermi--Lowdin orbitals*, J. Chem. Phys., **154**, 084112 (2021). DOI: 10.1063/5.0031341
18. Q. Xu, A. Sharma, and P. Suryanarayana, *M-SPARC: Matlab-Simulation Package for Ab-initio Real-space Calculations*, Software X, **11**, 100423 (2020). DOI: 10.1016/j.softx.2021.100709
19. Q. Xu, P. Suryanarayana, and J. E. Pask, *Discrete discontinuous basis projection method for large-scale electronic structure calculations*, J. Chem. Phys., 149, 094104 (2018). DOI: 10.1063/1.5037794
20. S. Ghosh and P. Suryanarayana, *Higher-order finite-difference formulation of periodic Orbital-free Density Functional Theory*, J. Comput. Phys., 307, 634-652 (2016), DOI: 10.1016/j.jcp.2015.12.027

Introducing the NIST Data and AI-Driven Materials Science Group

Lead Investigator: Francesca Tavazza, francesca.tavazza@nist.gov
Group Members: Brian DeCost, Laura Espinal, Howie Joress, A. Gilad Kusne, Austin McDannald, Zachary Trautt
Participating Institutions: NIST
Source of Support: NIST
Website: https://www.nist.gov/mml/mmsd/data-and-ai-driven-materials-science-group
Keywords: Autonomous Laboratories, Artificial Intelligence, Machine Learning, FAIR Data, High-Throughput Experimentation

Project Scope

The recently created NIST Data and AI-Driven Materials Science Group develops methods, algorithms, data, and tools, to accelerate the discovery, development, commercialization, and circularity of industrially relevant materials. We enable the trustworthy use of data and AI-driven methodologies within both experimental and computational materials science and engineering workflows. This poster will describe objectives of the group, summarize relevant findings of a recent workshop, and discuss future projects and plans. We are presenting a poster to make the MGI community aware of our existence (as a new group within NIST) to facilitate new collaborations and partnerships.

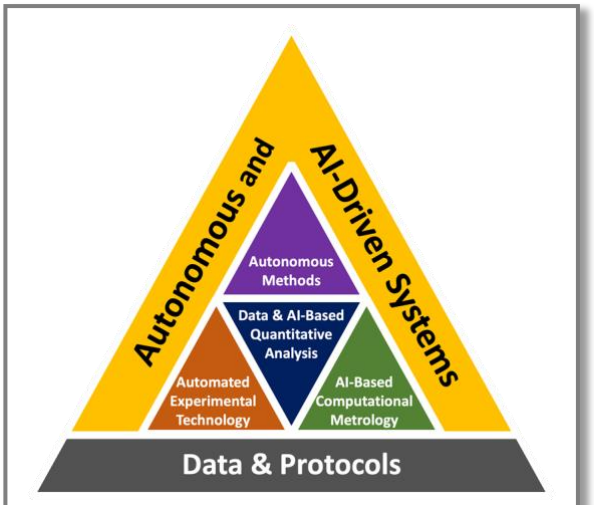


Figure: Graphical representation of core capabilities of the NIST Data and AI-Driven Materials Science Group.

Relevance to MGI

The MGI is a federal multi-agency initiative for discovering, manufacturing, and deploying advanced materials twice as fast and at a fraction of the cost compared to traditional methods. The NIST Data and AI-Driven Materials Science Group was founded in 2023 and has a mission that is aligned to the goals of MGI. Our work is focused on developing Autonomous Methods that form the core decision-making capability of self-driving laboratories, as well as robust automated Data and AI-Based Quantitative Analysis. We work on a diverse portfolio of materials characterization techniques, with a particularly strong focus on AI-Based X-Ray and Neutron Scattering Techniques. Similarly, we work on Automated Experimental Technology consisting of robotic and high-throughput experimental infrastructure to enable the rapid synthesis and characterization of materials. Furthermore, we develop machine learning algorithms to perform rapid and accurate selection of optimal system features, therefore optimizing performance, as well as material discovery, under a variety of conditions. Finally, Data and Protocols serve as a foundation and connective tissue for all our efforts. We have aligned our work in support of community adoption of the FAIR Data Principles. Machine actionable data is a critical enabler of data-intensive science and engineering.

Technical Progress

Prior to creation of the Data and AI-Driven Materials Science Group, the members of the group had an extensive publication history at NIST in topics related to high throughput experimentation, machine learning, autonomous experimentation, uncertainty quantification, and materials data infrastructure. Select publications are listed in Publications and References.

Future Plans

The group will continue to focus on autonomous experimentation in material science, specifically concentrating on:

- Direct Air Capture (DAC) of CO_2 from the atmosphere: Effective CO_2-sequestration requires suitable materials for DAC, which are difficult to find. The group is developing an autonomous, high throughput materials synthesis robotic system, and related ML algorithms and characterization capabilities, to expedite such a search. Metal–organic framework (MOFs) systems are the porous materials currently under investigation.
- Development of autonomous platforms for high-speed X-ray diffraction (XRD) measurements to probe the atomic structure of materials. The bottleneck to knowledge generation from these measurements is the analysis, which, in many cases, is still a completely manual process. Work in this program focuses on developing AI tools to optimize the amount of data to be collected as well as to replace the manual analysis with algorithmic data pipelines, to improve robustness, efficiency, and reproducibility.

Broader Impacts and Workforce Development

Members of the NIST Data and AI-Driven Materials Science Group have actively engaged in workforce development for some time. For nearly a decade group members have co-sponsored the Machine Learning for Materials Research Bootcamp [https://www.nanocenter.umd.edu/events/mlmr/] as well as collaborated closely with Prof. Takeuchi at University of Maryland in the development of a LEGO-based robot for teaching artificial intelligence to college students. (https://energy.umd.edu/news/story/legolas-participates-atnbspus-senate-robotics-showcase-on-capitol-hill). More recently, members of the group are actively engaged in the MaRDA FAIRtrain Working Group, which is working to embed FAIR Data Principles into Materials Science and Engineering Curriculum [https://github.com/marda-alliance/FAIRtrain].

Data Management and Open Access

Members of the NIST Data and AI-Driven Materials Science Group are actively involved in a number of working groups furthering the definition and adoption of the FAIR data principles. Group members actively participate in RDA [https://www.rd-alliance.org/], MaRDA [https://www.marda-alliance.org/], and the FAIR Digital Objects Forum [https://fairdo.org/].

Advancing Along the Materials Development Continuum and Partnerships to Translation

The NIST Data and AI-Driven Materials Science Group works side-by-side with industry stakeholders. We are disseminating our code at https://github.com/usnistgov/hermes

Publications and References

N/A

Collaborative Research: DMREF: Topologically Designed and Resilient Ultrahigh Temperature Ceramics

Lead Investigator: Gregory B. Thompson, gthompson@eng.ua.ed
Participating Institutions: University of Alabama, University of California San Diego, Colorado State University.
Source of Support: NSF-DMREF Nos. 2323456, 2323457, and 2323458
Website: none
Keywords: Fracture, Creep, Microstructural Engineering, Ultrahigh Temperature Ceramics

Project Scope

The overarching goal of this project is to design ultrahigh temperature ceramics (UHTCs) that are tough, that is resistant to fracture at low temperatures, and strong at high temperatures, that is being creep resistant. This will be achieved by utilizing low symmetry crystal structures with designed elongated shapes that fit together to create an interlocked material microstructure.

Relevance to MGI

This project meets the Materials Genome Initiative (MGI) by tightly integrating materials synthesis with materials characterization and modeling to produce microstructure architectures that facilitate improvements in toughness and creep resistance. Modeling accelerates the experimental choices of dopants that control surface energies which then facilitates stabilized shape morphologies. Based on our computational informed dopants, tailored powder synthesis techniques are leveraged to create a 'bottom-up' approach in making these materials into an interlocking microstructure. Through structural and chemical characterization, the dopant-microstructure linkage is verified with forward fed data that further improves the model predictions. This allows for a rapid convergence of material chemistries with targeted microstructure design.

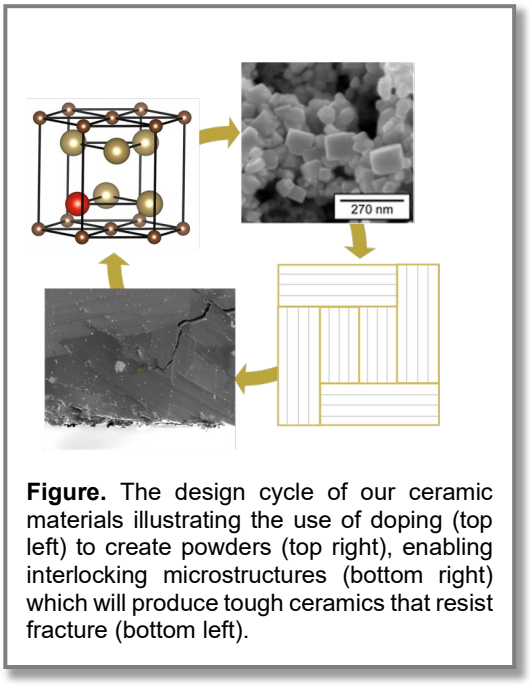


Figure. The design cycle of our ceramic materials illustrating the use of doping (top left) to create powders (top right), enabling interlocking microstructures (bottom right) which will produce tough ceramics that resist fracture (bottom left).

The microstructural selection will be further optimized by developing new models of microstructure-based fracture that is coupled with machine learning from 3D datasets of crack propagation. This will accelerate input information to the models garnered from the mechanical tests coupled with 3D characterization. Collectively, this will improve the predictive capability of the models that leads to optimized microstructures with enhanced mechanical performance.

Technical Progress

As this is the first year of this DMREF, our effort on each aspect – modeling, characterization/testing, and synthesis - is just beginning. Noting prior literature for the need for anisotropic morphologies for microstructure toughening, we have started with the trigonal Ta_2C phase because of its anisotropic crystal symmetry. We have successfully synthesized Ta_2C at UC San Diego from starting materials of tantalum chloride powder, carbon black, and the reaction reducing agent lithium. Depending on the chemical control and process condition, we can vary these powders from TaC to Ta_2C demonstrating engineering capability for our future design.

We have also made significant progress in the modeling of both Ta_2C doping as well as models of fracture at Colorado State University. Specifically, we have developed a new computer program that develops the

predicted shape of lower symmetry, *e.g*. trigonal crystals, from the surface energies. To date, previous codes only report cubic systems or hexagonal systems. In alignment with MGI initiatives, we plan to release this code on Github. We have also completed a comprehensive study of cleavage energies in tantalum carbides for our fracture models. These values are critical inputs to the microstructure-based fracture models we will develop. This cleavage energy work has been recently published as an invited paper in the *Journal of the American Ceramic Society* [1].

Finally, our materials testing and characterization efforts at the University of Alabama are progressing well. We have used a combination of focus ion beam (FIB) milling with scanning electron microscopy (SEM) to create multiple serial sectioned volumes of crack propagation initiated by indentation into the metal carbides. These images are now under analysis with our machine learning collaborator, Dr. Mireya S. García at the Instituto Politecnico Nacional (Mexico), to create synthetic microstructures. From these synthetic microstructures, we will support the microstructure-fracture modeling verification and validation, accelerating our design space for improving the fracture toughness through microstructure control. In addition, we have used the FIB to make a series of microcantilever beams in different oriented grains of Ta_2C and performed conditional fracture toughness tests. By creating these beams in individual grains, we have essentially 'single crystal' samples to experimentally evaluate to better understand the cleavage characteristics in this hemicarbide that then validates the models under development.

Future Plans

We will be extending our models of particle shape to include dopants of transition metals to control the shape anisotropy of the hemicarbide powder. The most promising compositions will be synthesized to make the powders using the aforementioned solvothermal synthesis technique with the powder morphology characterized to compare its shape to the modeling predictions. Through this comparison, we will improve our models that direct the team towards specific aspect ratios that lead to higher toughness. Specifically, we will develop a fracture model that relates microstructure to changes in fracture toughness with an emphasis on the number of easy cleavage planes that influence crack propagation.

Broader Impacts and Workforce Development

The training of our next generation workforce is being implemented in two main efforts. The first is the integration and training of the students in our DMREF. All students, currently four graduate research assistants and three undergraduates, meet every three weeks (or more) via Zoom with the faculty, related postdocs and staff, and our international machine learning collaborators where they provide a presentation of results stimulating a collective discussion among the team members. This is teaching them presentation skills, organizational planning, and technical communication. The other training efforts include the bi-national summer participation of high school and undergraduate students in the ENLACE program held at UC San Diego as well as the ASM International Materials Camp for secondary school instructors at UA.

Data Management and Open Access

As this project is in its first year, we are starting to develop the infrastructure to share data. Our main effort to this effect will be the development of a non-oxide ceramic database to accumulate and store data and allow it to be searchable. This platform will be hosted at UC San Diego. All relevant data produced by this effort will be stored there. The database will also be a compendium of published data on the properties of non-oxide ceramics.

Advancing Along the Materials Development Continuum and Partnerships to Translation

This effort is accelerating ceramic material development by targeting a desired property though microstructure control derived from the initial powder morphology. Hence, modeling directs proper chemistries to tailor powder synthesis from which experimental testing and characterization confirm this interaction and outcome. The acceleration is occurring by using modeling to guide powder synthesis to then guide microstructural engineering. As these outcomes develop in the subsequent years, interest in this approach will matriculate to both powder vendors and end use manufactures that require UHTCs for energy and defense applications.

Publications and References

1. S. Hossain, G. B. Thomson, and C. R. Weinberger, E*xploring fracture anisotropy in tantalum carbide compounds: A density functional theory approach*, Journal of the American Ceramic Society **In Press**, 1-12 (2024). DOI: 10.1111/jace.19917

ID4: Institute for Data Driven Dynamical Design

Lead Investigator: Eric Toberer, etoberer@mines.edu
Participating Institutions: CSM, UIUC, Princeton, Harvard, Tufts, Northeastern, Northwestern, WashU, Drexel, UCF, UCLA, Kebotix
Source of Support: NSF-HDR Institute
Website: https://www.mines.edu/id4/
Keywords: structural metamaterials, metal-organic frameworks, ion conductors, photocatalysis, generative models, atomistic simulation, uncertainty-aware workflows, visualization, diversity, active learning, autodifferentiation

Project Scope
ID4 aims to transform the design cycle for scientists and engineers. From chemistry to civil engineering, we seek to create platforms that accelerate the discovery of new mechanisms and dynamics through the complementary union of human and machine intelligence. By revolutionizing the design cycle (Figure 1) of molecules, materials, and structures, ID4 will reveal new mechanisms for fabrication and function across length scales. Specifically, we focus on these four domain areas: 1) superionic conductors, 2) reconfigurable metamaterials and lattice systems, 3) photochemical reactions, and 4) metal-organic frameworks.

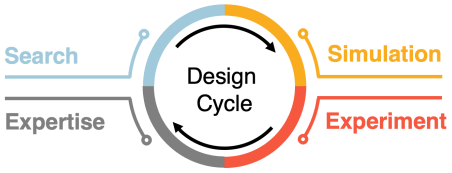


Figure 1. ID4 seeks to develop advances across the materials design cycle to enable the next generation of materials design.

Relevance to MGI
ID4 unites physical scientists and engineers with data and computer scientists to create transformative AI/ML methods for the chemistry, materials, and structures domains. Core to ID4 is broadly distributing these methods through open-source software and cyber-infrastructure, and serving as a nexus to enable knowledge transfer to the broad community. Within each domain area of ID4, the ultimate goal is a workflow that links every step of the design cycle. Workflows are comprised of building blocks that require foundational developments in AI/ML. Each of the four challenges areas are at tipping points where foundational developments in AI/ML are expected to provide transformative advances.

Technical Progress

The ID4 team has made significant advances in workflow components. Here, we highlight one advance from each location within the design cycle.

Search - **Symmetry aware generative model:** To automate the inverse design of crystalline materials, we have designed an energy-based Generative Flow Network for crystals that leverages crystallographic space groups and symmetries for crystal recommendation. The model combines continuous and discrete sampling to learn from on-the-fly black-box rewards, devised a new representation of crystalline materials which eliminates modeling degeneracies induced by crystallographic symmetries, and developed a new graph neural network architecture for more efficient model training.

Simulation - **Ion transfer mechanisms:** Molecular dynamics using ML force fields identifies new mechanism for proton transfer in solid acids, 'proton slingshot mechanism', involves both polyanion rotation and O-H bond reorientation for completing long-range proton hopping in solid acid compounds. To validate the simulations, we experimentally examined the hydrogen position in superprotonic structure of $Cs_2(HSO_4)(H_2PO_4)$, and found the simulation and experimental results were in good agreement. This approach can be used to design new electrolyte materials that leverage this mechanism.

Experiment - **Synthesis of MOFs:** Natural language processing methods were developed for the extraction of synthesis procedures of MOFs from the vast corpus of literature and databases. We have also digitally archived a collection of ten years of research on the synthesis of MOFs from the Uribe-Romo group, including synthesis data

of small molecules, building blocks and intermediates, as well as attempts at MOF/COF crystallization, including many failed experiments. The data in this archive are being translated into ML-ready data. Both of these efforts will allow the prediction of synthesis procedures for hypothetical MOFs.

Expertise – **Visualization platform:** Dimbridge software platform was developed to allow users to gain more insight from dimensional reduction methods when applied to high dimensional data. One example is predicate view trends, where users can select a trajectory in the low-dimensional projections and look at trends across the trajectory in the dimensions that most strongly drove the original projection. Three of our four domain areas are beta-testing this software.

Future Plans
Looking to the future, ID4 will focus on developing the individual components for four workflows on: 1) superionic conductors, 2) reconfigurable metamaterials and lattice systems, 3) photochemical reactions, and 4) metal-organic frameworks. Seedling projects in these areas include machine-learnt coarse graining of superionic conduction dynamics, symmetry-aware learning of mechanical metamaterials via equivariant neural network flows, developing neural nets for many body simulations, developing probabilistic workflows for material design with an initial focus on high entropy alloys, and minimizing construction waste through ML-enabled sequential design.

Broader Impacts and Workforce Development
We aspire to create the next generation of leaders by exposing students at all levels to multidisciplinary science that bridges between data science and challenges in the physical sciences and engineering. One way we accomplish this is by hosting high school, community college, and 4-year undergraduate students for research experiences in ID4 groups. For K-12 students, we provide school-based coding clubs, summer coding camps, science demo days (e.g. teaching about material properties using chocolate), and support for the US Crystal Growing Competition. Through our efforts, we reached over 600 students at the K-16 level in the last year.

We are additionally hosting a series of workshops, open to the greater computational materials science community, on topics spanning cross-cutting foundations of data science, data-intensive research in science and engineering, and education and workforce development. Past and upcoming workshops include: 1) the 2nd annual NSF Harnessing the Data Revolution (HDR) Ecosystem Conference 2) Interactive Visualization and Analysis of High-Dimensional Scientific Data, 3) AI-Ready Data: Navigating the Dynamic Frontier of Metadata and Ontologies, 4) Integration of Data Fluency into 6th-12th Grade Education, and 5) Machine Learning and Monte Carlo Methods for the Quantum Many-Body Problem.

Data Management and Open Access
The ID4 website, (https://www.mines.edu/id4/papers-codes) serves as a central directory for distributed team member github repos; we have opted to use a distributed model (rather than a single ID4-wide repo) for code still under development to avoid issues with version control. Within these repos, effort has been made to include tutorial datasets and training datasets. ID4 expects FAIR data practices across the member groups.

Advancing Along the Materials Development Continuum and Partnerships to Translation
To maximize the transformative potential of ID4, we have cross-cutting data objectives that link different scientific objectives. To date, we have developed 19 software tools and 2 databases, all of which are available to the scientific community. ID4 additionally includes one company, Kebotix, as part of our Institute. Kebotix is able to suggest new materials for ID4 to explore and provide feedback on what ID4 products are industrially relevant.

Publications

1. Q. Nguyen and A. B. Dieng, *Quality-Weighted Vendi Scores and Their Application to Diverse Experimental Design*, International Conference on Machine Learning (2024). DOI: 10.48550/arXiv.2405.02449
2. S. Liu, P. Ramadge, and R. P. Adams, *Generative Marginalization Models*, International Conference on Machine Learning (2024). DOI: 10.48550/arXiv.2310.12920
3. J. Qu, Y. R. Xie, K. M. Ciesielski, C. E. Porter, E. S. Toberer, E. Ertekin, *Leveraging Language Representation for Materials Exploration and Discovery*, npj Comp. Mater. **10,** 58 (2024). DOI: 10.1038/s41524-024-01231-8
4. R. Oval, R. Pastrana, E. P. G. Bruun, V. Paris, S. G. Aviño, S. Adriaenssens, and W. Al Asali. *An Integrated Digital Design and Construction Approach for Falsework-Minimal Masonry Vaults*, Structures **63**, 106428 (2024). DOI: 10.1016/j.istruc.2024.106428
5. A. K. M. A. Shawon, W. Guetari, K. Ciesielski, R. Orenstein, J. Qu, S. Chanakian, Md. T. Rahman, E. Ertekin, E. S. Toberer, and A. Zevalkink, *Alloying-Induced Structural Transition in the Promising Thermoelectric Compound CaAgSb*, Chem. Mater. **36**, 1908 (2024). DOI: 10.1021/acs.chemmater.3c02621
6. C. L. Rom, A. Novick, M. J. McDermott, A. A. Yakovenko, J. R. Gallawa, G. T. Tran, D. C. Asebiah, E. N. Storck, B. C. McBride, R. C. Miller, A. L. Prieto, K. A. Persson, E. Toberer, V. Stevanović, A. Zakutayev, and J. R. Neilson, *Mechanistically Guided Materials Chemistry: Synthesis of Ternary Nitrides, CaZrN2 and CaHfN2*, J. Am. Chem. Soc. **146**, 4001 (2024). DOI: 10.1021/jacs.3c12114
7. G. Xiong, L. S. Wang, and S. M. Haile, *Superprotonic conductivity in RbH2−3y(PO4)1−y: a phosphate deficient analog to cubic CsH2PO4 in the (1 − x)RbH2PO4 – xRb2HPO4 system*, Mater. Horiz. **10**, 5555 (2023). DOI: 10.1039/D3MH00852E
8. R. Pastrana, D. Oktay, R. P. Adams, and S. Adriaenssens, *JAX FDM: A differentiable solver for inverse form finding*, International Conference on Machine Learning (2023). DOI: 10.48550/arXiv.2307.12407
9. S. Monadjemi, M. Guo, D. Gotz, R. Garnett, and A. Ottley, *Human-Computer Collaboration for Visual Analytics: an Agent-based Framework*, EuroVis (2023). DOI: 10.1111/cgf.14823
10. A. Pasarkar, G. Bencomo, S. Olsson, and A. B. Dieng, *Vendi Sampling for Molecular Simulations: Diversity As A Force For Faster Convergence and Better Exploration*, J. Chem. Phys. **159**, 144108 (2023). DOI: 10.1063/5.0166172
11. A. Novick, E. Toberer, V. Stevanović, Q. Nguyen, and R. Garnett, *Simulating high-entropy alloys at finite temperatures: An uncertainty-based approach*, Phys. Rev. Materials **7**, 063801 (2023). DOI: 10.1103/PhysRevMaterials.7.063801
12. D. Oktay, E. Medina, M. Mirramezani, and R. P. Adams, *Neuromechanical Autoencoders: Learning to Couple Elastic and Neural Network Nonlinearity*, International Conference on Learning Representations (2023). DOI: 10.48550/arXiv.2302.00032
13. Y. An, J. Greenberg, A. Kalinowski, X. Zhao, X. Hu, F. J. Uribe-Romo, K. Langlois, J. Furst, and D. A. Gómez-Gualdrón, *Knowledge Graph Question Answering for Materials Science (KGQA4MAT)*, Metadata and Semantics Research Conference (2023). DOI: 10.48550/arXiv.2309.11361
14. M. Islamov, H. Babei, R. Anderson, K. B. Sezginel, J. R. Long, A. J. H. McGaughey, D. A. Gomez-Gualdron, and C. E. Wilmer, *High throughput screening of hypothetical metal-organic frameworks for thermal conductivity*, npj Comp. Mater. **9,** 11 (2023). DOI: 10.1038/s41524-022-00961-x
15. Q. Nguyen, and R. Garnett. *Nonmyopic Multiclass Active Search with Diminishing Returns for Diverse Discovery*. International Conference on Artificial Intelligence and Statistics, PMLR **206**, 5231 (2023).
16. J. Li, and S. A. Lopez, *Excited-state distortions promote the photochemical 4π-electrocyclizations of fluorobenzenes via machine learning accelerated photodynamics simulations*, Chem A Euro J. 28, e202200651 (2022). DOI: 10.1002/chem.202200651
17. B. Deng, A. Zareei, X. Ding, J. C. Weaver, C. H. Rycroft and K. Bertoldi, *Inverse design of mechanical metamaterials with target nonlinear response via a neural accelerated evolution strategy*, Adv. Mater. **34**, 2206238 (2022). DOI: 10.1002/adma.202206238
18. A. E. Forte, P. Z. Hanakata, L. Jin, E. Zari, A. Zareei, M. C. Fernandes, L. Sumner, J. Alvarez, and K. Bertoldi, *Inverse Design of Inflatable Soft Membranes Through Machine Learning*, Adv. Funct. Mater. **32**, 2111610 (2022). DOI: 10.1002/adfm.202111610
19. R. Chang, Y.-X. Wang and E. Ertekin, *Towards overcoming data scarcity in materials science: unifying models and datasets with a mixture of experts framework*, npj Comp. Mater. **8**, 242 (2022). DOI: 10.1038/s41524-022-00929-x
20. T.-W. Liu, Q. Nguyen, A. B. Dieng, and D. A. Gomez-Gualdron, *Diversity-driven, efficient exploration of a MOF design space to optimize MOF properties: application to NH3 adsorption*. Submitted. DOI: 10.26434/chemrxiv-2024-fqll9

RDA: Harmonised Terminologies and Schemas for FAIR Data in Materials Science and Related Domains Working Group

Contact: Zachary Trautt, zachary.trautt@nist.gov
Group Chairs: Gerhard Goldbeck, Zachary Trautt, Iseult Lynch, Leah McEwen, Masashi Ishii, Kwang-Ryeol Lee
Participating Institutions: Research Data Alliance
Source of Support: NIST
Website: https://www.rd-alliance.org/groups/harmonised-terminologies-and-schemas-fair-data-materials-science-and-related-domains-wg/
Keywords: FAIR Data, Schemas, Ontologies, Terminologies, Vocabulary

Project Scope

The focus of this Research Data Alliance (RDA) Working Group (WG) is on increasing uptake of the FAIR Principles in materials research (in particular in connection with Interoperability and Reusability), supported by improved resources, in particular widely-agreed and FAIR terminologies, metadata and ontologies. While the main focus of the WG is in the material sciences, close interactions with cognate domains, in particular chemistry, are crucial in order to avoid conflicting approaches and also to utilize and integrate with already existing semantic artefacts and resources in these fields. This poster will present the objectives of this WG, present current progress, and solicit participation from the MGI community. Interested parties can join the group via the RDA website or contact Zachary Trautt for help.

Figure: Logo of the Research Data Alliance

Relevance to MGI

Materials data is one of the three original core elements of the MGI Venn Diagram. While there has been tremendous progress for some narrowly-defined problems (e.g., OPTIMADE for computational data, NeXus Data Format for neutron, x-ray, and muon science), significant challenges remain for the broader materials science and engineering community. To address these challenges, an international group of experts has launched a new WG within RDA. This group has the title of "Harmonised terminologies and schemas for FAIR data in materials science and related domains WG".

Technical Progress

The WG has authored a case statement [1], which has been subject to peer review of the RDA community and is recognized and endorsed by the RDA Secretariat. The group kicked-off its formal working activities in May 2024 during the RDA 22nd Plenary Meeting. The group holds monthly working meetings to maintain progress on its working streams:

- Stream A: Collection, review and FAIR maturity assessment of the existing semantic artefacts.
- Stream B: Best practices for materials science practitioners to achieve FAIR data based on terminologies, schema, ontologies
- Stream C: Elaborate harmonized terminologies and schema in materials sciences
- Stream D: Adoption: Demonstrate FAIR terminologies, schema and ontologies

Work has commenced on Stream A and Stream B. Work on Stream C and Stream D will occur in the future and will leverage outputs from the other streams.

Future Plans

The group will meet monthly to continue to work on planned outputs. Participation from the MGI community is welcome and encouraged. The group has the following planned outputs:

1. A review and FAIR maturity assessment of the existing semantic artefacts landscape (terminologies, taxonomies, schema, ontologies) for materials science and related domains; producing a documentation of the process of FAIR maturity review, application and elaboration of semantic resources for the domain.
2. Best practice recommendations for materials science practitioners to improve FAIR data based on terminologies, schema, ontologies documented in A, including how to apply the FAIR principles within the context of publishing semantic artefacts in the domains of this WG.
3. New, harmonized semantic artefacts (in particular terminologies and schema) required to improve FAIR maturity in the domains of this WG.

Broader Impacts and Workforce Development

Education and workforce development are not within the scope of this working group. However, all RDA working groups work in collaboration with other groups both within and beyond RDA. Given the importance of education and workforce development, we will certainly partner with groups working on this critical need.

Data Management and Open Access

The FAIR data principles are a core focus area of the RDA and this working group. MGI projects are encouraged to actively participate in the broader RDA as well as this working group. There are many groups in RDA that are relevant to the MGI community.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The planned outputs of this working group are well-aligned with MGI. Many reports continue to describe a lack of data FAIRness as a major bottleneck for data-driven materials science and engineering.

Publications and References

1. G. Goldbeck, K.R. Lee, Z.T. Trautt, L. McEwen, M. Ishii, I. Lynch, *Harmonised terminologies and schemas for FAIR data in materials science and related domains WG - Case Statement*, Research Data Alliance (2024). URL: https://www.rd-alliance.org/rationale/harmonised-terminologies-and-schemas-fair-data-materials-science-and-related-domains-wg/rev-002/

DMREF: Designing Linked Gel Networks with Tunable Valence

Lead Investigator: Thomas Truskett, truskett@che.utexas.edu
Participating Institutions: University of Texas at Austin, New York University, NIST
Source of Support: NSF-DMREF
Website: http://sites.utexas.edu/LinkedGelsDMREF
Keywords: dynamic bonding, colloids, polymer networks, coarse-grained modeling, plasmonic nanocrystals

Project Scope

We are combining experimental nanoscience and organic chemistry, modeling, and theory to produce design principles for gel materials with desired morphological, optical, and rheological properties.[1] Our strategy is to harness multifunctional linking molecules to assemble controlled-valence networks formed from nanoparticles or star polymers through use of complementary functional groups that participate in dynamic covalent bonding. Simulations and theory will lead to predictions for how emergent gel properties depend on molecular linker reactivity and network connectivity, which will feed back into the design of the kinetics and thermodynamics of the bonding moieties.

Relevance to MGI

We are following a data-driven approach well-aligned with MGI principles, where experimental results are used to inform simulation model development. Models are then used to predict which macroscopic or molecular parameters can be changed to alter gel properties. Our effective collaboration is facilitated through sub-group and all-hands meetings, a project-wide Slack, and use of data sharing resources. The team (PI: Truskett; co-PIs: Beaucage, Hocky, Milliron, and Rosales) is strengthened by diverse backgrounds spanning chemistry, chemical engineering, physics, and materials science, allowing us to combine expertise at molecular, nano, and macroscopic length scales to tailor the design of our materials from the bottom up.

Technical Progress

Based on theoretical predictions of equilibrium phase boundaries and pathways for gel formation in limited-valence colloids, we are pursuing new strategies for assembling dynamically bonded networks of macromer or nanocrystal building blocks. Initial experimental characterization of the phase behavior and shear rheology of tetra-functional and octa-functional poly(ethylene glycol) (tetraPEG and octaPEG) macromers has helped us to identify favorable dynamic chemistries for reversible assembly as well as knowledge gaps in network microstructures (e.g., defectivity) that models could help address. The results also clarified aspects about molecular resolution necessary to accurately model assembly across the relevant length and time scales. Our efforts aim to uncover fundamental principles for rationally tuning gelation pathway and bulk properties of dynamic hydrogels assembled via reversibly linked, (directly or statistically) controlled-valence colloids/macromolecules.

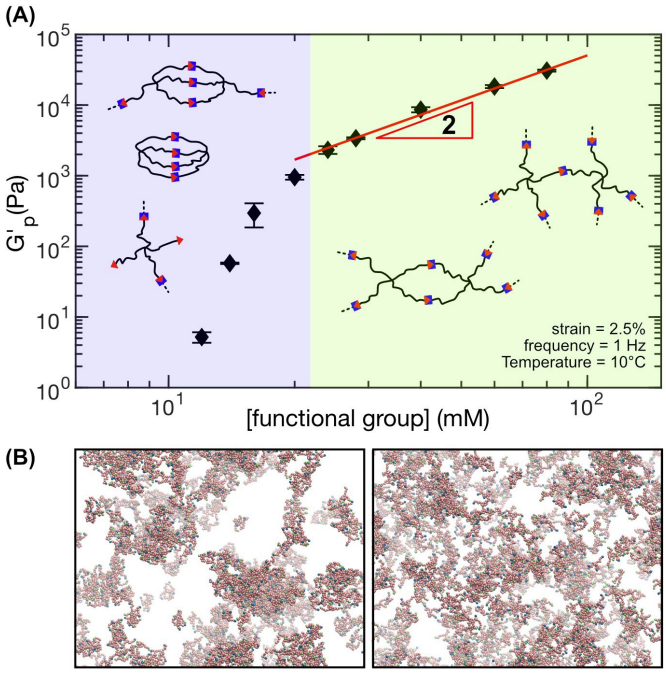


Figure 1. (A) Measured shear plateau modulus vs macromer concentration for dynamic tetraPEG (5 kDa) hydrogels at 10°C. Changes in bonding motifs and network connectivity are reflected in concentration-dependent scaling of modulus. (B) Heterogeneous (left) and homogeneous (right) macromer networks formed in coarse-grained tetraPEG simulations.

Future Plans
Emulsion-imaging techniques will be developed to quantify liquid-liquid phase boundaries and gel formation paths and combined with high-throughput analysis of network structuring via X-ray and neutron scattering to validate our simulation models and test new molecular thermodynamic theories for assembly. Conventional rubber elasticity theory cannot describe the observed trends in dynamic tetraPEG hydrogels; our results will clarify the roles of tunable network topology and dynamic covalent bonding in the mechanical response of these materials and linked nanocrystal gels. We will leverage the specificity and tunability of dynamic chemistries (e.g., monofunctional capping agents directed to specific linkers or macromers/colloids) to inhibit or promote targeted bonding motifs. The ability of our models to predict such post-synthetic modifications to valence will provide a stringent test of the design principles we learn.

Broader Impacts and Workforce Development
Through an iterative approach to design, test, understand, and improve the gel networks, our DMREF team is training graduate students, postdoctoral scholars, and undergraduate researchers to be nimble and effective members of the R&D workforce. Our experimental scientists are learning to develop robust and reproducible strategies for data generation pipelines, and our computational team is collaborating across institutions to develop and release high-quality simulation and analysis software. These tools will be shared as open-source code and will enhance the ability of other researchers to design crosslinked gel materials. Each summer, we mentor research projects for undergraduates from community colleges and four-year universities. So far on this project, Truskett has mentored one student through the Chemical Research At Texas (CREATE) program at UT Austin, and Hocky has mentored one student through the Research Experiences for Peruvian Undergraduates. We have launched a transfer-year interest group (TrIG) to help community college transfer students navigate their transition to studies in Chemical Engineering at UT Austin. Finally, we are developing curricula to decrease the barrier for students to use computation and simulation tools in chemistry and chemical engineering.

Data Management and Open Access
Simulation codes, input files, and analysis scripts will be published on GitHub alongside an open-source workflow module that allows for consistent re-creation and advancement of simulated model systems. All simulation codes have been crafted with two main guiding principles beyond those associated with good research practices (such as accuracy, repeatability, etc.): ease of use and intuitive comprehension. These two principles promote the accessibility required for others to make meaningful advancements by building on this work. Experimental and simulation data will be made available upon publication, primarily in the form of Supplementary Material including extensive examples of computational and experimental data and methods in addition to information about accessing data on our project and research groups' websites. Digital data and code will be further archived in a repository such as Zenodo to produce a DOI, and data will be findable via links within publications and from our groups' and collaboration websites.

Advancing Along the Materials Development Continuum and Partnerships to Translation
MGI principles are enabling rapid progress on this project, as we are extending theoretical and computational predictions from equilibrium gels of patchy colloids to generate novel designs for polymer networks. Without the support for a multi-faceted multi-PI collaboration, this would not be possible. We will use the experimental results to validate and refine a unified framework for linked assembly of network-based materials. The open-source workflow module we are creating for computation-guided design via coarse-grained simulations will be made publicly available. In later stages of the project, materials with useful photonic or biocompatible functionalities could be patented and result in synergistic opportunities to collaborate with industry to optimize these materials for applications, and Truskett, Milliron, and Rosales have previous experience in this regard.

Publications and References

1. Z. M. Sherman, D. J. Milliron, and T.M. Truskett, *Distribution of Single-Particle Resonances Determines Plasmonic Response of Disordered Nanoparticle Ensembles*, ACS Nano, in revision (2024)

DMREF: Accelerated discovery of metastable but persistent contact insecticide crystal polymorphs for enhanced activity and sustainability

Lead Investigator: Mark E. Tuckerman, mark.tuckerman@nyu.edu
Participating Institutions: New York University
Source of Support: NSF-DMREF
Website: https://www.crystalmathatnyu.org
Keywords: molecular crystals, phase transformations, metastability, crystal engineering, infectious diseases

Project Scope

Contact insecticides are an essential component in the fight against vector-borne infectious diseases, such as malaria. Previous work from the NYU laboratory has revealed an inverse correlation between the activity of contact insecticides and the thermodynamic stability of their polymorphs. The overarching challenge is the discovery of metastable crystal forms with high kinetic stability, which ensures that highly active crystal polymorphs persist in these structures for the duration of their use. This project aims to develop an integrated experimental-theoretical framework for the accelerated discovery of polymorphs that meet these criteria.

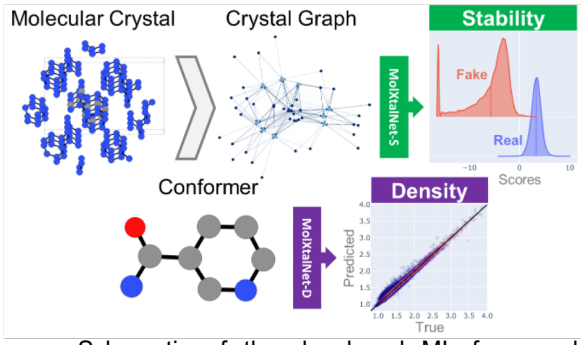


Figure. Schematic of the developed ML framework, MXtalTools, for stability ranking and property prediction. The structure of the molecular crystal is represented by a crystal graph neural network which is trained on the Cambridge Structural Database to score 'fake' vs. 'real' crystal structures (top). Furthermore, the model can predict crystal densities given a molecule conformer (bottom).

Relevance to MGI

The project relies on a continuous and mutual feedback among theory, computation, and experiment in three key areas: (i) discovery of thermodynamically accessible polymorphs, (ii) assessment of kinetic stability and transformation pathways, and (iii) evaluation and control of surface properties. Following initial experimental results on polymorphism for various compounds, several theoretical frameworks have been developed that aid the prediction of crystal structures, the stability ranking of polymorphs, crystal property predictions, and classification of local structural features. These computational tools form a basis for the identification of thermodynamically accessible polymorphs and the evaluation of their relative kinetic stabilities against phase transformations. Leveraging collaboration between experiment and theory, we are focusing on the impact of additives on polymorph selectivity and stability. The experimentally observed trends are rationalized with advanced molecular simulations. Subsequently, the simulation results are analyzed to extract common features and topological motifs that can be used to inform the experimental search for new polymorphs and crystallization protocols. Eventually, the integrated experimental and theoretical framework will serve as the basis for the accelerated exploration of a larger library of target compounds.

Technical Progress

Key results of our methodological developments include a topological crystal structure prediction (CSP) framework, a molecular graph neural network for property prediction and stability ranking, a point-cloud autoencoder for molecule representation, and a machine learning (ML) model to classify local structural environments in molecular crystals. The topological CSP is based on two main principles regarding correlations between a molecule's principal axes of inertia and its orientation in the unit cell and between atom types and special positions within the unit cell. Generated structures based on these principles are optimized for close contacts by minimizing an objective function to adhere to optimal values determined from a statistical analysis of the Cambridge Structural Database (CSD), thereby eliminating the need for expensive energy evaluations. We successfully tested our approach for insecticide compounds. Using tools from geometric deep learning of molecular graphs, we have developed an ML framework,

MXtalTools, trained on the CSD to predict densities and provide a stability score for molecular crystals. This is particularly useful as a fast filter to significantly reduce the number of proposed structures in the initial search stage of a CSP workflow without energy computations. In a second approach to CSP for molecular crystals, we are actively developing computational and machine learning tools with the specific aim of quickly identifying all the polymorphic structures into which a given molecule may realistically crystallize. Here, the question of efficient data representation is one of the most important aspects. To represent intramolecular degrees of freedom together with the overall 3D orientation of a given molecule, we developed the first multi-type O(3) equivariant point-cloud autoencoder, which can be pre-trained on large molecular datasets. This representation is general and maps the full information contained in the original molecular structure. To analyze polymorphism in molecular crystals, we have developed two complementary ML models to classify local structural environments. One approach utilizes graph neural networks (GNN) and the other molecular symmetry functions (SF) to represent the systems. Whereas the molecular SF classifier requires expertly handcrafted input features for each molecule, the GNN is able to learn an efficient data representation for the local molecular environment based on the raw atom types and coordinates. Both models are easily trained, exhibit high classification accuracy, and provide a general approach for the analysis and interpretation of simulation data in molecular solids, which will be particularly useful for the study of structural transformations, including nucleation and growth. Our joint experimental and theoretical efforts have recently focused on the role of additives in polymorph selectivity and stability. For acridine, a compound revealing eight polymorphs, 14 additives were investigated experimentally of which 7 had a substantial effect on polymorphism. We are currently performing molecular simulations of crystalline clusters embedded in a melt ('seeding approach') to investigate the relative stability of different polymorphs as a function of additives. This will be combined with the experimental results to inform the targeted design of specific polymorphs.

Future Plans

We will continue our efforts in developing a microscopic understanding of how additives impact the stability and transformation between different polymorphs in molecular crystals. We have now established several examples where we observe clear changes in the crystallization behavior as well as the transformation between different polymorphs. Eventually, we aim to be able to suggest new additives that trigger the formation of specific polymorphs, and also inhibit or promote transformations between polymorphs. Here, we will utilize the methods and software developed in this project and aim to establish a direct feedback loop between theory and experiment.

Broader Impacts and Workforce Development

Postodocs, graduate students, and undergraduate students are involved in the project and have the opportunity to learn theoretical and experimental state-of-the-art methodologies. On the theory side, they are trained, specifically, in statistical mechanics, enhanced sampling, and machine learning approaches. On the experimental side, they acquire knowledge in crystallization techniques, polymorph screening methods, powder X-ray diffraction, Raman spectroscopy, and hot stage polarized light microscopy. The acquired skills are not only beneficial within an academic context but also lay the basis for a highly qualified workforce in industry. In collaboration with the New York Theatre Ballet School we organized a visit of ten students ages 8-13 to NYU, during which we discussed ideas regarding the formation of crystals, symmetries, and transformations. Subsequently, six girls choreographed a ballet dance inspired by the theme of crystal polymorphism. A video of their performance is available on our website.

Data Management and Open Access

We have launched a website, www.crystalmathatnyu.org, that includes links to our software repositories and databases, a compilation of insecticide crystal structures discovered by NYU investigators, with links to the respective Crystallographic Information Files, publications, an insecticide crystal image gallery, and information regarding our outreach activities.

Advancing Along the Materials Development Continuum and Partnerships to Translation

In the context of contact insecticides, the accelerated discovery of metastable polymorphs with enhanced efficacy can reduce the amount of toxicant needed and, thereby, also reduce the environmental impact. Our findings should be readily transferable to other fields where the properties of metastable forms can also be exploited, including pharmaceutical industry and other areas of materials science. The software tools we are creating have utility beyond the current DMREF project and are likely to help accelerate the development of materials through crystal engineering for use in organic electronics, energetic materials, and pharmaceuticals at the pre-clinical stage.

Publications and References

1. N. Fellah, L. Tahsin, C. Jin Zhang, B. Kahr, M.D. Ward, and A.G. Shtukenberg, *Efficient Polymorph Screening through Crystallization from Bulk and Confined Melts*, Cryst. Growth Des. **22**, 7527-7543 (2022). DOI: 10.1021/acs.cgd.2c01065
2. M. Kilgour, J. Rogal, and M.E. Tuckerman, *Geometric Deep Learning for Molecular Crystal Structure Prediction*, J. Chem. Theory Comput. **19**, 4743-4756 (2023). DOI: 10.1021/acs.jctc.3c00031
3. R. Aronin, P. Brázda, L.N. Smith, C.J. Zhang, J.B. Benedict, Z.Y. Marr, B. Rybtchinski, H. Weissman, A.G. Shtukenberg, and B. Kahr, *Chlorfenapyr Crystal Polymorphism and Insecticidal Activity*, Cryst. Growth Des. **24**, 1284-1292 (2024). DOI: 10.1021/acs.cgd.3c01257
4. A.G. Shtukenberg, D.E. Braun, M. Tan, N. Fellah, and B. Kahr, *Suppression of Disorder in Benzamide and Thiobenzamide Crystals by Fluorine Substitution*, Cryst. Growth Des. **24**, 5276-5284 (2024). DOI: 10.1021/acs.cgd.4c00517
5. B. Erriah, A.G. Shtukenberg, R. Aronin, D. McCarthy, P. Brázda, M.D. Ward, and B. Kahr, *ROY Crystallization on Poly(ethylene) Fibers, a Model for Bed Net Crystallography*, Chem. Mater. **36**, 2432-2440 (2024). DOI: 10.1021/acs.chemmater.3c03188
6. D. Kuroshima, M. Kilgour, M.E. Tuckerman, and J. Rogal, *Machine Learning Classification of Local Environments in Molecular Crystals*, J. Chem. Theory Comput., accepted (2024). DOI: 10.48550/arXiv.2404.00155
7. M.E. Tuckerman and N. Galanakis, *Topological Crystal Structure Prediction*, Nat. Commun., under review (2024). DOI: 10.21203/rs.3.rs-3361974/v1
8. M. Kilgour, M.E. Tuckerman, and J. Rogal, *Multi-Type Point Cloud Autoencoder: A Complete Equivariant Embedding for Molecule Conformation and Pose*, NeurIPS, under review (2024). DOI: 10.48550/arXiv.2405.13791

DMREF: Collaborative Research: Developing Damage Resistant Materials for Hydrogen Storage and Large-scale Transport

Lead Investigator: T. A. Venkatesh, t.venkatesh@stonybrook.edu
Participating Institutions: Stony Brook University, Stanford University, Massachusetts Institute of Technology
Website: none
Keywords: Hydrogen embrittlement, fatigue, dislocation dynamics, atomistic simulation, machine learning.

Project Scope

This project aims to: (1) develop a physics-based modeling platform based on hydrogen interaction with crystalline defects at both atomistic and microstructural scales, informed by and integrated with experiments, to accelerate the pace of discovering controlling mechanisms of hydrogen embrittlement under fatigue; (2) enable faster development of hydrogen resistant materials in the energy transportation sector as it transitions from the transport of fossil fuels such as natural gas to hydrogen based renewables.

Relevance to MGI

This project is designed to advance our knowledge of crack tip processes that control damage accumulation and propagation under fatigue loading, and the role of hydrogen in making the material more brittle (Figure 1). We hypothesize that the controlling mechanisms occur in the plastic zone around the crack tip, over a length scale of about 1 to 10 microns, which is too small for continuum theory to be predictive and too large for atomistic simulations to handle by brute-force. We close this knowledge gap at the mesoscale, through a tightly coupled experimental-computational program. Our multi-scale modeling efforts build upon the recent advances made in atomistic simulations (at Sandia National Laboratory/Stanford), dislocation dynamics simulations (at Stanford), with insights on crystal plasticity (from MIT) and continuum level modeling (from Stony Brook).

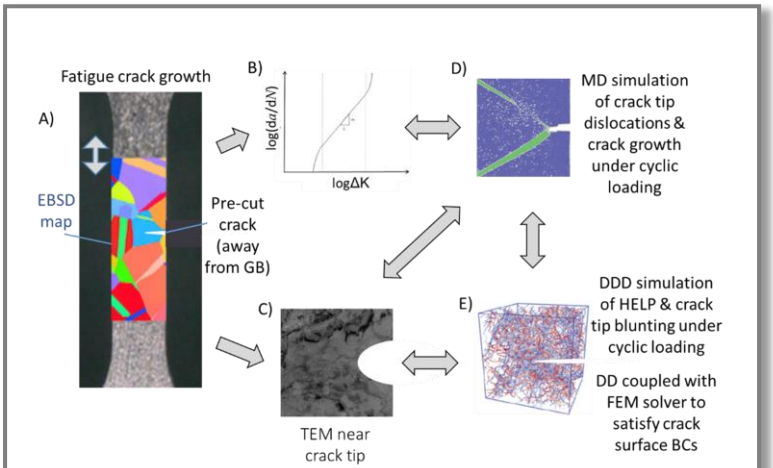


Figure 1. Schematic illustrating: A) An oligo-crystalline pipeline steel sample with a pre-cut crack being tested under cyclic fatigue load for crack growth; the overlapped EBSD map showing orientations of individual grains. B) The crack growth rate (d*a*/d*N*) observed in Stages I, II and III. C) TEM examination of the dislocations near the crack tip. D) MD simulation to study crack tip plasticity and crack growth under cyclic loading with influence of hydrogen. E) Dislocation dynamics (DD) simulation of hydrogen induced shear localization and crack tip deformation.

Technical Progress

With a view towards enabling a wide set of stakeholders to make informed decisions about the roll-out of the hydrogen economy, a study was conducted to review the current status and implementation of hydrogen blending in natural gas pipeline networks [1]. The primary emphasis of this review was to highlight top-level state-of-knowledge across various stages in the lifecycle of a hydrogen economy—from methods for hydrogen production, to transportation of hydrogen blends and end-use applications. A computational fluid dynamic model has been developed to quantify frictional losses and energy efficiency of transport of methane-hydrogen blends across straight pipe sections [2, 3]. It is observed that, in general, an increase in the energy costs is expected when hydrogen, with its lower density, is transported along with methane (which has higher density) in various blend ratios. The state-of-the-art in invoking multi-scale modeling for understanding hydrogen effects in materials has been reviewed [4]. Molecular dynamic (MD) simulations have been invoked to study hydrogen (H) adsorption as

well as its effects on the strength of pearlitic steels [4]. In particular, the effects of H on the strength of the cementite (Fe_3C)/ferrite interphase and the ferrite/ferrite grain boundaries, have been investigated.

Future Plans

We will use high-throughput nano-indentation experiments under different hydrogen environments to calibrate our atomistic-DD model. We will use experiments and simulations of cyclic tensile tests to clarify the dislocation mechanisms in the limit of very low stress intensity factor amplitude (ΔK), where the hydrogen effects have not been conclusively determined or understood. We will examine the fatigue crack growth rate (da/dN), with the emphasis on the question of why hydrogen effects require a critical value of ΔK to be fully developed. We will develop physics-based continuum level models for hydrogen effects on fatigue crack growth to create reliable engineering roadmaps for life prediction and risk assessment for hydrogen storage and transport structures.

Broader Impacts and Workforce Development

This project will lead to broad impact at several levels: (i) By advancing our current understanding of the influence of hydrogen interactions with dislocations on the mechanisms associated with fatigue crack growth in pipeline steels, the proposed research activity will provide scientific and technological impact in the hydrogen storage and transport industry; (ii) This project will educate, train and mentor graduate and undergraduate students, and postdoctoral associates and will provide a platform for promoting science to a broader audience, including under-represented minorities and high school students; (iii) The simulation tools, database and interactive visualization tools will be made widely available through online portals to facilitate dissemination and education; (iv) A major 6-day symposium with over 150 presentations was co-organized with hydrogen program leaders from NREL and Sandia National Laboratory to facilitate the dissemination of knowledge in the areas of advanced materials for hydrogen and fuel cell technologies to a world-wide community. (v) The DMREF team hosted a Hydrogen Education Day at SBU, presided over by the Provost, for 100+ participants from the energy industry, labor, government officials and several Senators and Assembly Members from NY State attended the event.

Data Management and Open Access

The source code of the atomistic and dislocation dynamics simulation programs developed in the project will be released to the public: http://micro.stanford.edu/wiki/MD++_Manuals. We will also develop wiki pages that fully describe the steps needed to reproduce the computation results in our publications. The wiki pages include all the input files necessary for reproducing all the numerical results/data. We will deposit experimental data and Abaqus input (.inp) and results (.fil) files in ascii format in DSpace@MIT and Stony Brook's Academic Commons, which will be accessible to the general public.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We are working closely with our industry collaborators such as National Grid in this project who will help identify the commercialization potential for some of the fundamental insights obtained in this project.

Publications and References

1. D. Mahajan, K. Tan, T. A. Venkatesh, P. Kileti, and C. Clayton, *Hydrogen Blending in Gas Pipeline Networks – A Review*, ***Energies***, 15 (10), 3582, (2022).
2. K. Tan, D. Mahajan and T. A. Venkatesh, *Computational fluid dynamic modeling of methane-hydrogen mixture transportation in pipelines: estimating energy costs*, ***MRS Advances***, (2022).
3. K. Tan, D. Mahajan and T. A. Venkatesh*, *Computational Fluid Dynamic Modeling of Methane-Hydrogen Mixture Transportation in Pipelines: Understanding the Effects of Pipe Roughness, Pipe Diameter and Pipe Bends*, ***International Journal of Hydrogen Energy***, 49, 1028-1042, (2024).
4. G. Cheng*, X. Wang, K. Chen, Y. Zhang, T. A. Venkatesh*, X. Wang, Z. Li and J. Yang, *Probing the Effects of Hydrogen on the Materials used for Large-scale Transport of Hydrogen through Multi-scale Simulations*, ***Renewable and Sustainable Energy Reviews***, 182, 113353, (2023).
5. X. Wang, Y. Zhao, G. Cheng, Y Zhang, T. A. Venkatesh, *Hydrogen adsorption in phase and grain boundaries of pearlitic steels and its effects on tensile strength*, ***MRS Advances***, (2022).

QMC-HAMM: High accuracy multiscale models using quantum Monte Carlo

Lead Investigator: Lucas Kyle Wagner,lkwagner@illinois.edu
Participating Institutions: University of Illinois at Urbana-Champaign
Source of Support: DOE-BES
Website: qmc-hamm.github.io.
Keywords: first principles calculations, quantum Monte Carlo, multiscale modeling, machine learning, effective Hamiltonian.

Project Scope

We seek to improve the quality of multiscale models based on high accuracy first principles calculations. QMC-HAMM leverages the quantum Monte Carlo class of methods, which directly treat electron correlation. Materials systems studied include hydrogen at high pressure, layered 2D materials, and ionic conductors. We focus on improving input data for models learned from first principles , and rigorous evaluation of uncertainties in the models.

Relevance to MGI

Computational data is at the core of MGI efforts, as well as relating this data to large length scale models (theory). Our collaboration provides packages and methods to improve the quality of the underlying computational data used in MGI and to better relate the information from those data to predictions of the behavior of materials.

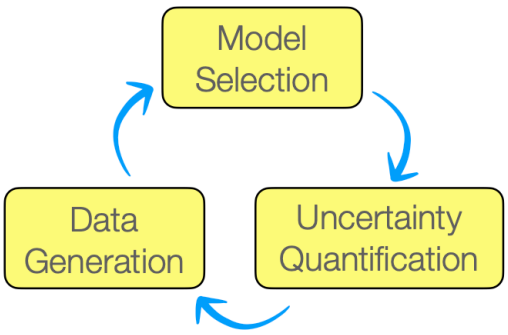


Figure. Data generation is done using high accuracy methods, which is used to select large length-scale models. Uncertainty quantification is then used to identify whether quantity or quality of data is required to improve the models, and to provide confidence intervals on the predictions.

Technical Progress

Graphene Twisted bilayer graphene, and other stackings of graphene, have been observed to exhibit several unusual electronic phases, some of which appear to be indicative of strong electronic interactions. The minimum number of atoms that can be used to model this system number in the tens of thousands, out of reach for standard first principles methods. Over the past few years, it has become clear that corrugations in the layers due to the Moire' patterns are critical in determining the electronic properties of the system. To model these corrugations accurately, an accurate treatment of van der Waals interactions is required, which is an electron correlation effect. In Ref 7, we used quantum Monte Carlo methods, implemented in the TCMP-supported QMCPACK package, to evaluate the van der Waals interactions in graphene layers as a function of the relative coordinates of the layers. We then used this data to fit an atomic potential that included the very high accuracy interactions. In Ref 14, we used feature selection techniques from machine learning to learn an electronic tight-binding model from first principles calculations. This model treats the changes in electronic behavior on stretching and bending the graphene much more accurately than previous models, as we show in the paper. These modes are critical in understanding the effects of corrugation on the electronic behavior of layered graphene. We have also found (Ref 5) several unusual new corrugation patterns at low energy in bilayer graphene. As mentioned above, all the models and data supporting this work are available through our website and are being made available on the Materials Data Facility.

New phases of hydrogen. The primary interest of this application area is the determination of the phase diagram at high pressure over a large range of temperatures. In Ref 6, we used quantum Monte Carlo simulations to derive an atomistic potential accurate across multiple phases of hydrogen. These simulations resulted in the discovery of a new potential phase in hydrogen at high pressure and temperature, as shown in Fig 2. As part of the

hydrogen project, we have published the QMC data on our website and in the Materials Data Facility. This data will be helpful in developing models of both electrons in hydrogen and in developing atomic-level models.

Methods development and improvement. While computation of coarse-grained atomistic potentials from high accuracy first principles quantum data is well-known, the same is not true for the computation of interacting electronic models. In Ref 10, we take a step towards achieving this goal for a test system, vanadocene, which emulates a correlated defect in a material. Such defects are responsible for the color of many gemstones, as well as a potential platform for quantum information processing. However, understanding the many-electron states of these defects remains challenging. We performed a cross-method benchmark of effective models from this system, using quantum Monte Carlo and quantum chemistry methods as reference, and learned guidelines for electronic model creation.

Future Plans

Graphene: We are working to incorporate a learned model for electronic interactions into a model. This new model will thus include a complete description of coarse-grained electronic interactions, one-body terms, and lattice motion. We plan to use this model to investigate electron-phonon effects and correlated electron phases in this system, using a very accurate reference.

Hydrogen: We are using hydrogen as a testbed for optimal learning algorithms and uncertainty quantification of models derived from Monte Carlo data. We are also investigating the capability of machine-learning models to describe solid-liquid phase transition accurately.

Methods development: We plan to extend our systematic approach to electronic models to a number of defects relevant to quantum information in collaboration with the MiCCom collaboration.

Broader Impacts and Workforce Development

This project has resulted in 5 completed PhDs, and currently supports 3.5 PhD positions and 2 postdoctoral associates. These students and postdocs are trained in the latest methods both in computational simulation for materials and data-based strategies. These students and postdocs have migrated to postdoctoral positions in other fields, where they apply their skills; for example, in national labs, industry, and other university environments.

Data Management and Open Access

A list of data from our collaboration is available here: https://qmc-hamm.github.io/data/. This central location for our collaboration makes it easier for researchers who see our talks to find our data. That is, if someone knows one of us, our data is easy to find. We have published most of our data in collaboration with the Materials Data Facility, which has a search function that enhances findability. Models and code that we produce are available using the Python Package Index, which is a large database of packages that allow for very easy installation. We are working with a software engineer at the National Center for Supercomputing Applications to make the trained models produced as a part of our collaboration available in a similar way.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The main outcome of our project is to improve the predictive ability of computational methods for materials. This is done by using high-accuracy quantum Monte Carlo calculations on which to base models of materials. The upshot of this for materials discovery is that a major difficulty in finding new materials by design is that standard density functional methods are not sufficiently accurate. The lack of accuracy can lead to false positive rates over 90% for tasks like thermodynamic stability. This false positive rate can waste experimental resources. If the methods and models we use are adopted, we can reduce the false positive rate significantly.

Publications and References

[1] A. C. Tyner and S. Sur, *Dipolar Weyl Semimetals*, Phys. Rev. B **109**, L081101 (2024). https://doi.org/10.1103/PhysRevB.109.L081101.

[2] S. Sur, Y. Xu, S. Li, S.-S. Gong, and A. H. Nevidomskyy, *Field Induced Non-BEC Transitions in Frustrated Magnets*, Phys. Rev. Lett. **132**, 066701 (2024). https://doi.org/10.1103/PhysRevLett.132.066701.

[3] D. M. Ceperley, S. Jensen, Y. Yang, H. Niu, C. Pierleoni, and M. Holzmann, *Training Models Using Forces Computed by Stochastic Electronic Structure Methods*, Electron. Struct. **6**, 015011 (2024). https://doi.org/10.1088/2516-1075/ad2eb0.

[4] W. A. Wheeler et al., *PyQMC : An All-Python Real-Space Quantum Monte Carlo Module in PySCF*, J. Chem. Phys. **158**, 114801 (2023). https://doi.org/10.1063/5.0139024.
[5] T. Rakib, P. Pochet, E. Ertekin, and H. T. Johnson, *Helical Dislocation in Twisted Bilayer Graphene*, Extreme Mechanics Letters **63**, 102053 (2023). https://doi.org/10.1016/j.eml.2023.102053.
[6] H. Niu, Y. Yang, S. Jensen, M. Holzmann, C. Pierleoni, and D. M. Ceperley, *Stable Solid Molecular Hydrogen above 900 K from a Machine-Learned Potential Trained with Diffusion Quantum Monte Carlo*, Phys. Rev. Lett. **130**, 076102 (2023). https://doi.org/10.1103/PhysRevLett.130.076102.
[7] K. Krongchon, T. Rakib, S. Pathak, E. Ertekin, H. T. Johnson, and L. K. Wagner, *Registry-Dependent Potential Energy and Lattice Corrugation of Twisted Bilayer Graphene from Quantum Monte Carlo*, Phys. Rev. B **108**, 235403 (2023). https://doi.org/10.1103/PhysRevB.108.235403.
[8] M. Holzmann, F. Calcavecchia, D. M. Ceperley, and V. Olevano, *Static Self-Energy and Effective Mass of the Homogeneous Electron Gas from Quantum Monte Carlo Calculations*, Phys. Rev. Lett. **131**, 186501 (2023). https://doi.org/10.1103/PhysRevLett.131.186501.
[9] V. Gorelov, Y. Yang, M. Ruggeri, D. M. Ceperley, C. Pierleoni, and M. Holzmann, *Neutral Band Gap of Carbon by Quantum Monte Carlo Methods*, Condens. Matter Phys. **26**, 33701 (2023). https://doi.org/10.5488/CMP.26.33701.
[10] Y. Chang et al., *Downfolding from Ab Initio to Interacting Model Hamiltonians: Comprehensive Analysis and Benchmarking of the DFT+cRPA Approach*, Npj Comput Mater **10**, 1 (2024). https://doi.org/10.1038/s41524-024-01314-6.
[11] S. Yuan, Y. Chang, and L. K. Wagner, *Quantification of Electron Correlation for Approximate Quantum Calculations*, J. Chem. Phys. **157**, 194101 (2022). https://doi.org/10.1063/5.0119260.
[12] T. Rakib, P. Pochet, E. Ertekin, and H. T. Johnson, *Moiré Engineering in van Der Waals Heterostructures*, Journal of Applied Physics **132**, 120901 (2022). https://doi.org/10.1063/5.0105405.
[13] T. Rakib, P. Pochet, E. Ertekin, and H. T. Johnson, *Corrugation-Driven Symmetry Breaking in Magic-Angle Twisted Bilayer Graphene*, Commun Phys **5**, 1 (2022). https://doi.org/10.1038/s42005-022-01013-y.
[14] S. Pathak, T. Rakib, R. Hou, A. Nevidomskyy, E. Ertekin, H. T. Johnson, and L. K. Wagner, *Accurate Tight-Binding Model for Twisted Bilayer Graphene Describes Topological Flat Bands without Geometric Relaxation*, Phys. Rev. B **105**, 115141 (2022). https://doi.org/10.1103/PhysRevB.105.115141.
[15] K. K. Ly and D. M. Ceperley, *Stability and Distortion of Fcc LaH10 with Path-Integral Molecular Dynamics*, Phys. Rev. B **106**, 054106 (2022). https://doi.org/10.1103/PhysRevB.106.054106.
[16] K. K. Ly and D. M. Ceperley, *Phonons of Metallic Hydrogen with Quantum Monte Carlo*, J. Chem. Phys. **156**, 044108 (2022). https://doi.org/10.1063/5.0077749.
[17] H. Lu, S. Sur, S.-S. Gong, and D. N. Sheng, *Interaction-Driven Quantum Anomalous Hall Insulator in a Dirac Semimetal*, Phys. Rev. B **106**, 205105 (2022). https://doi.org/10.1103/PhysRevB.106.205105.
[18] T. Rakib, E. Ertekin, P. Pochet, and H. T. Johnson, *An Efficient Computational Framework for Charge Density Estimation in Twisted Bilayer Graphene*, Computational Materials Science **199**, 110746 (2021). https://doi.org/10.1016/j.commatsci.2021.110746.
[19] S. Pathak, B. Busemeyer, J. N. B. Rodrigues, and L. K. Wagner, *Excited States in Variational Monte Carlo Using a Penalty Method*, J. Chem. Phys. **154**, 034101 (2021). https://doi.org/10.1063/5.0030949.
[20] S. Pathak and L. K. Wagner, *A Light Weight Regularization for Wave Function Parameter Gradients in Quantum Monte Carlo*, AIP Advances **10**, 085213 (2020). https://doi.org/10.1063/5.0004008.

DMREF-2323752: Magneto-electro-optically coupled hybrid metamaterial thin film platform for photonic integrated circuits

Lead Investigator: Haiyan Wang (hwang00@purdue.edu)
Co-Investigators: Edwin García, Peter Bermel, Minghao Qi
Participating Institutions: Purdue University
Source of Support: NSF-DMREF
Website: https://nanohub.org/groups/dmref
Keywords: hybrid metamaterials, photonic integrated circuits, vertically aligned nanocomposites, magneto-optical coupling

Project Scope

The DMREF-Purdue team works on the design, process and integration of complex hybrid metamaterials thin films for photonic integrated circuits (PICs). Specifically, our work focuses on the understanding of electro-optical and magneto-optical coupling effects in complex nanoscale hybrid metamaterials with a two-phase hybrid thin film platform to harness the coupling mechanisms between charges, spins, and photons. The ***technological goal*** is to demonstrate several key building blocks for future large-scale PICs, including highly-efficient and integrated optical switches, nonreciprocal devices, and magneto-optic sensors for PICs, as a proof of concept for this new hetero-integration paradigm.

Relevance to MGI

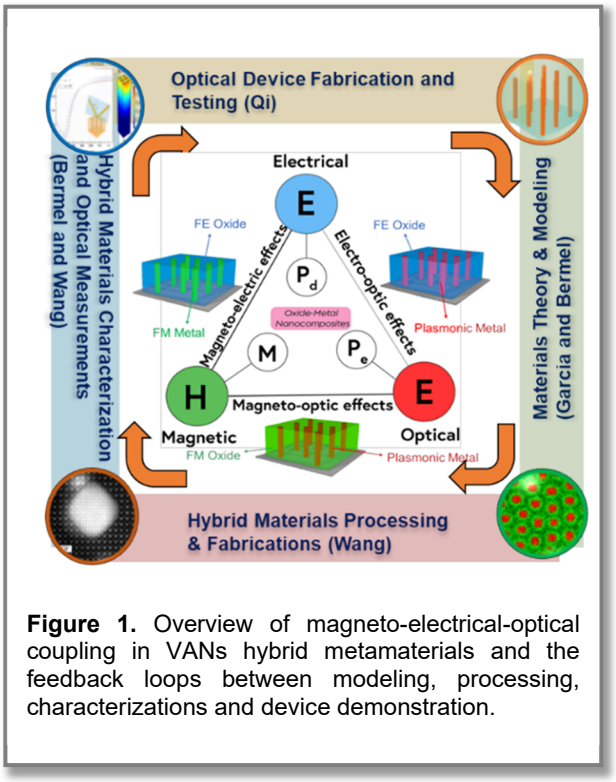


Figure 1. Overview of magneto-electrical-optical coupling in VANs hybrid metamaterials and the feedback loops between modeling, processing, characterizations and device demonstration.

As shown in Fig.1, we work on integrating hybrid thin film growth, phase-field modeling, electromagnetic modeling, optical device fabrication and testing, and demonstrate magneto-electric-optical coupling in a coherent feedback loop, as a combined theory-synthesis-characterization approach. This combined approach will expedite metamaterials discovery more than any single approach would on its own. There is an enormous variety of materials combinations, nanopillar ordering, and geometries that may provide interesting optical properties and exciting opportunities for discovering novel metamaterials and phenomena. This theory-guided materials screening process, combined with a device-driven approach, will accelerate materials discovery by providing systematic investigation of the electromagnetic properties of hybrid film geometries and the complex alloy pillar designs for enhanced property coupling. For example, Phase-field modeling can take hours if not days, even when using state-of-the-art algorithms and systems, due to the small spatiotemporal resolutions on which they operate. In contrast, our team has recently developed an advanced customized Graphical Processing Unit (GPU)-based Finite Element Method (FEM) scheme to accelerate the solution of Partial Differential Equations (PDE). By directly integrating experimental data analytics and accelerated physical modeling, we develop a data-driven physics-based modeling infrastructure that can quantify the properties and degradation in metamaterials in minutes, rather than in months or years. We will integrate untapped GPU computing strategies, ML algorithms, and well-established data analytics to set the stage for data-driven materials discovery.

Technical Progress

Progress in the first year highlights the collaborative nature of the DMREF project:

1. We have demonstrated water-soluble VAN designs in Au-Sr3Al2O6 vertically aligned nanocomposite thin films for novel Au nanostructure integration on substrates. (Paper 1 in Next Nanotechnology 2024)
2. We have successfully grown a set of $BaTiO_3$-metal nanocomposite thin films on Si substrate for optical waveguide device demonstrations. Such device performance has been modeled using finite-difference time domain simulations using multilayer designs. (Wang, Qi, Bermel, paper in progress)
3. Detailed characterization of multilayer oxide material growth using variable-angle spectroscopy ellipsometry (Wang, Bermel, Paper submitted)
4. Using a sacrificial buffer design, free standing VAN hybrid metamaterial thin films have been demonstrated and transferred for device measurements. (Wang, Paper 2, 4, 7)
5. Via ML-accelerated phase diagram calculation, 3-element and 4-element complex phase diagrams have been developed for alloy-VAN designs in BaTiO3-metal based hybrid systems for enhanced coupling properties (Wang, Garcia, Paper 5, 6)

Future Plans

We are working on multiple facets of the project including optical waveguide demonstration using various VAN designs on Si, experimental validation of phase diagram calculations for complex alloy VAN formation, novel functionality demonstration in transferred VAN thin films and on-chip integration (paper 8 and others). Two very interesting directions evolve from the project are the sustainable deposition using recycled substrates and ML based VAN predictions using existing databased and unpublished results in the group. All of these directions are in line with the overall project goals in searching for highly integrable VAN hybrid metamaterials for PICs and practical integration for industry.

Broader Impacts and Workforce Development

We are working to address materials science education and workforce shortfalls by advancing cyber-physical curriculum and broadening participation of underrepresented minorities (URMs) in this field to grow the number of qualified individuals prepared to both accelerate MGI goals and enter the semiconductor workforce. 4 teams with 4 PIs, 5 Ph.D. graduates, 3 undergraduate researchers are working collaboratively. Students are trained with multidisciplinary skill sets covering thin film processing, materials modeling, device modeling and device processing and testing. We are also collaborating with the SCALE and READI semiconductor workforce development programs led by Purdue University to provide like-minded cohorts of students, special events with industry, specialty courses, and industrial internship experiences.

Data Management and Open Access

Besides journal publications, conference presentations, and patent applications, we are working to broadly disseminate and make accessible the multi-scale optical modeling methodology to a broad audience. These tools will be widely distributed to the scientific community through Purdue's NSF-supported nanotechnology dissemination site, nanoHUB (over 2 million unique users per year). Bermel and García have extensive experience developing these tools in collaboration with nanoHUB—their prior work to create or substantially improve simulation tools resulted in new tool publications on nanoHUB and substantive final reports. We have developed a team website for disseminate research findings to general public timely. We are also working with Purdue University Repository (PUR) for data storage, data sharing and research dissemination.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We are working to develop a large database for VAN based hybrid metamaterials with novel coupling properties and tunability for on-chip photonic integration. We envision that 1 or 2 hybrid metamaterials will be first adopted in certain PIC components as we are currently demonstrating. Next, we will integrate multiple hybrid metamaterials for a system-level PICs demonstration. These findings can offer alternative solutions to optical component companies. Our thin film transfer methods developed can be adopted by other semiconductor industries where epitaxial oxide growth is challenging. Our phase diagram modeling tools and machine learning algorithms for expedited phase diagram calculations can be adopted by other researchers in the field. The data generated can be directly adopted by others working in the complex metamaterial designs.

Publications and References

2024 (2 published, 1 accepted, 5 submitted and under review)

1. Benson Kunhung Tsai, Jiawei Song, Juncheng Liu, Jianan Shen, Yizhi Zhang, Xinghang Zhang, Haiyan Wang, Au Nanopillar Array Prepared by Selective Etching of Au-Sr3Al2O6 Vertically Aligned Nanocomposite Thin Films, ***Next Nanotechnology,*** 2024. https://doi.org/10.1016/j.nxnano.2024.100071
2. James P. Barnard, Jianan Shen, Benson K. Tsai, Yizhi Zhang, Max R. Chhabra, Aleem Siddiqui, Raktim Sarma, Haiyan Wang, Large Area Transfer of Bismuth-Based Layered Oxide Thin Films using a Flexible Polymer Transfer Method, ***Small Methods***, accepted, 2024.
3. Jianan Shen, Benson Kunhung Tsai, Yizhi Zhang, Ke Xu, James P. Barnard, Zedong Hu, Xinghang Zhang, Haiyan Wang, Van der Waals Epitaxy of Bismuth-Based Multiferroic Layered Supercell Oxide Thin Films Integrated on Flexible Mica Substrate, ***Small Science,*** 2024, https://doi.org/10.1002/smsc.202300244
4. James P. Barnard, Yizhi Zhang, Lizabeth Quigley, Jianan Shen, Benson K. Tsai, Max R. Chhabra, Jiho Noh, Hyunseung Jung, Oleg Mitrofanov, Raktim Sarma, Aleem Siddiqui, Igal Brener, Chloe F. Doiron, & Haiyan Wang Transfer of Epitaxial Strained Multiferroic Thin Films on Millimeter Scale using Rigid Substrate Epoxy Method, submitted, 2024.
5. Jijie Huang, Zedong Hu, Benson Tsai, Jialong Huang, Jianan Shen, Yizhi Zhang, James Barnard, Jiawei Song, and Haiyan Wang, Ultra-thin Ternary FeCoNi Alloy Nanoarray in BaTiO3 Matrix for Room-temperature Soft Magnets, Hyperbolic Metamaterial and Multiferroicity, submitted, 2024.
6. Juncheng Liu, Yizhi Zhang, Hongyi Dou, Benson Kunhung Tsai, Abhijeet Choudhury, and Haiyan Wang, Self-assembled TiN-metal nanocomposites integrated on flexible mica substrates towards flexible devices, submitted, 2024.
7. Jianan Shen, Lizabeth Quigley, James Barnard, Ping Lu, Benson Kunhung Tsai, Dmitry Zemlyanov, Yizhi Zhang, Xuanyu Sheng, Jeremy Gan, Matteo Moceri, Zedong Hu, Jialong Huang, Chao Shen, Julia Dietz, Xinghang Zhang, Haiyan Wang, Epitaxial Thin Film Growth on Recycled STO Substrates towards Sustainable Process of Complex Oxides, submitted, 2024.
8. Yizhi Zhang, Zedong Hu, Claire Amelia Mihalko, Lizabeth Quigley, Ping Lu, Julia Deitz, Debargha Paul, Benson Kunhung Tsai, Shiyu Zhou, Jianan Shen, Haiyan Wang, Introducing magnetic field into NbN superconductor by Co nanopillars, submitted, 2024.
9. Changkyun Lee, Jie Zhu, Jiawei Song, Haiyan Wang, Xiulin Ruan, Peter Bermel, "Temperature-dependent optical dispersion of composite Cerium oxide (CeO2) and Barium zirconate (BaZrO3) single layers and multi-layers," *Journal of Optics*, submitted, 2024

Collaborative Research: DMREF: Accelerated Discovery of Artificial Multiferroics with Enhanced Magnetoelectric Coupling

Lead Investigator: Li Yang, lyang@physics.wustl.edu
Participating Institutions: Washington University in St Louis, University of Texas, Austin, University of Nebraska-Lincoln
Website: none
Keywords: multiferroic, magnetoelectric coupling, *ab initio* simulation, van der Waals material, moiré superlattices

Project Scope

This project is to combine computational search and experimental fabrications and characterizations to search for and realize artificial multiferroics exhibiting enhanced magnetoelectric (ME) coupling by integrating two-dimensional (2D) van der Waals (vdW) magnets with ferroelectrics in two types of heterostructures: vdW/vdW and vdW/oxide heterostructures. Taking advantage of the nonvolatile polarization and piezoelectric effect in ferroelectrics, tunable magnetism in layered vdW materials, and substantial interface-to-volume ratio, we propose to achieve electrical control of the magnetic order, magnetic anisotropic energy (MAE), magnetic Curie or Néel temperature (T_C or T_N), and magnetic moiré pattern through interfacial coupling mechanisms.

Relevance to MGI

Artificial multiferroics offer a promising solution to achieve enhanced coupling between the ferroelectric (FE) and magnetic orders that are not available in single phase materials. Given that a large number of 2D magnetic and FE materials have already been predicted and grown, the possible combinations of these building blocks can reach the order of 10^4-10^5. It is thus imperative to launch a computation-led program to search for optimal artificial multiferroics, as shown in the right figure. A heterostructure needs to be computed as a whole system before re-evaluating the ferroic orders and their coupling. Experimental studies of prototypical heterostructures will be used to validate computational methods and guide improved designs. We will develop new high-throughput computational methods to identify about a few thousand suitable multiferroics. The interpretation of experimental observations will be elucidated by computations and complementary measurements. Ultimately, we aim to identify and realize ~10 new artificial multiferroics with figures of merit better than currently available ones in the following aspects: high ferromagnetic T_C or antiferromagnetic T_N, soft coercive field, tunable MAE, and modulation of magnetism at low switching voltage.

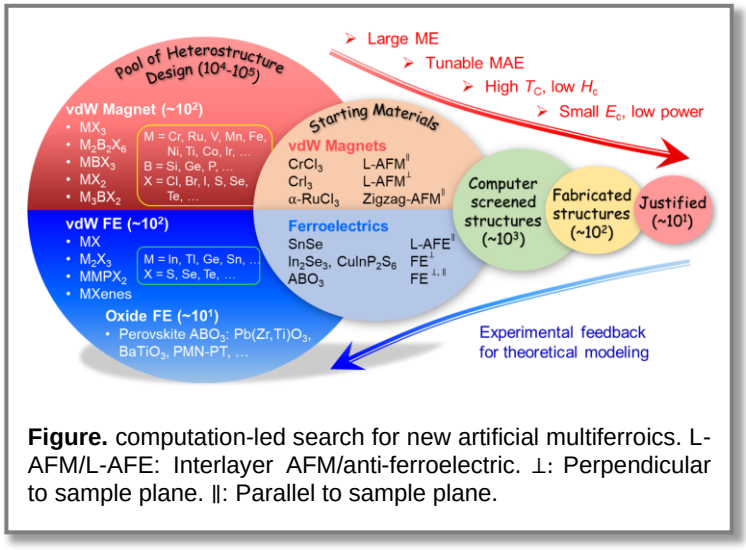


Figure. computation-led search for new artificial multiferroics. L-AFM/L-AFE: Interlayer AFM/anti-ferroelectric. ⊥: Perpendicular to sample plane. ∥: Parallel to sample plane.

Technical Progress

We have conducted data mining through several databases, including Material Project and 2D MatPedia, to identify appropriate vdW magnets and ferroelectric materials. Employing first-principles simulations of these candidates, we have predicted the promising heterostructures that may exhibit enhanced ME couplings. Our simulations also found a few insulating vdW heterostructures with enhanced ME or ferroic coupling, such as $PbZr_{0.2}Ti_{0.8}O_3$ (PZT)/$CrCl_3$ and PZT/$CuInP_2S_6$ heterostructures, which have been validated experimentally by Hong group. With theory guidance, we have synthesized promising vdW magnetic or ferroelectric materials, which will be the elements to construct the proposed multiferroic heterostructures and potentially enhanced MAE. We have employed a suite of complementary techniques, including Raman, scanning probe microscopy, and transport, to characterize the atomic structures, magnetotransport, and optical properties of the fabricated ferroic materials and heterostructures. Additionally, our collaboration has explored unusual and room-temperature robust moiré

ferroelectrics in twisted h-BN. The ferroelectric domain forms due to charge redistribution at the interface when a B atom is aligned with a N atom. Most interestingly, this charge redistribution leads to a periodic electrostatic potential that may be used to engineer the properties of an adjacent functional thin layer. Yang group showed this potential is described by a simple theory of electric polarization. The predictions are validated by Li group via Kelvin probe force microscopy. The ability to impose a periodic potential by the ferroelectric domain on a functional layer may prove to be a new way to realize multiferroic functionalities.

Future Plans

With the progress of growth and characterizing vdW magnetic and ferroelectric layers, we will aim to realize new artificial multiferroics with enhanced ME coupling by exploiting their unique interfacial interactions. More heterostructures made by vdW/vdW and vdW/oxides will be proposed by simulations to search for magnetoelectric properties. Meanwhile, experimental groups will further improve the PVT and CVD growth techniques to fabricate more vdW magnets (such as CrX_3 and $MnBi_2Te_4$) and ferroelectrics/piezoelectrics (such as SnSe and SnTe), as well as exploiting mechanical exfoliation of bulk samples, such as $CuInP_2S_6$. We will further make heterostructures of these materials to explore the strain and charge transfer in the interface and the magnetoelectric properties. Developed optical tools, including linear and nonlinear optical responses, will be combined with magnetotransport studies and scanning probe microscopy techniques, including piezoresponse force microscopy and magnetic force microscopy, to detect the magnetic and polarization orders in these heterostructures and moiré structures.

Broader Impacts and Workforce Development

Two undergraduate students, seven graduate students, and two postdocs have been supported by this program, including a female undergraduate student, a female Ph.D. student, a Hispanic postdoc, and a female postdoc. A graduate-level course, "First-principles studies of quantum materials", have been developed at Washington University in the spring semester of 2022. A Funsize Physics post based on synthesis of 2D $CrCl_3$, "The Future is Flat," has been created and posted online.

Data Management and Open Access

Our institutes (Washinton University in St Louis, University of Nebraska-Lincoln, and University of Texas-Austin) provide unlimited data storage space on one or more cloud-based servers. These servers are managed centrally on a long-term basis. The candidate structures can be publicly accessed via https://sites.google.com/view/cloqm/home/research/dmref-database?authuser=0.

Advancing Along the Materials Development Continuum and Partnerships to Translation

The project accelerates materials discovery and development through its combined theoretical and experimental approach. The computational search to identify candidate magnetic and ferroelectric materials and interfaces are continuously improved by feedback from material growth and characterizations. The developed nonlinear optical characterization not only provides an efficient tool to characterize magnetic orders but also helps theoretical simulations to reveal the fundamental physics mechanism behind the magnetoelectric coupling.

Publications and References

1. K. Lai, "Spontaneous polarization in van der Waals materials: Two-dimensional ferroelectrics and device applications", J. Appl. Phys. 132, 121102 (2022). DOI: 10.1063/5.0116445

2. Y. Lu, Y. Wang, L. Zhu, L. Yang, L. Wang, "Electric Field Tuning of Magnetic States in Single Magnetic Molecules", Phys. Rev. B 106, 064405 (2022). DOI: 10.1103/PhysRevB.106.064405

3. W. Yang, L. Zhu, Y. Lu, E. Henriksen, L. Yang "Point Defects in Two-Dimensional $RuCl_3$", Phys. Rev. Materials 7, 064004 (2023). DOI: 10.1103/PhysRevMaterials.7.064004

4. J. Wang, Z. Ahmadi, D. Lujan, X. Li, J.E. Shield, and X. Hong, "Physical Vapor Transport Growth of Antiferromagnetic CrCl3 Flakes Down to Monolayer Thickness", Advanced Science 10, 2203548 (2023). DOI: 10.1002/advs.202203548

5. D. Li, X. Hong, *et al.*, "Ferroelectric Domain Control of Nonlinear Light Polarization in MoS2 via PbZr0.2Ti0.8O3 Thin Films and Free-Standing Membranes", Advanced Materials 35, 2208825 (2023). DOI: 10.1002/adma.202208825

6. K. Wang, D. Li, J. Wang, Y. Hao, H. Anderson, L. Yang, and X. Hong, "Interface-Tuning of ferroelectricity and quadruple-well state in CuInP2S6 via ferroelectric oxide", ACS Nano, in press (2023). DOI: 10.1021/acsnano.3c03567

7. D.S. Kim, L. Yang, X. Li, *et al.*, "Anisotropic excitons reveal local spin chain directions in a van der Waals antiferromagnet", Advanced Materials 35, 2206585 (2023). DOI: 10.1002/adma.202206585

8. D.S. Kim, L. Yang, X. Li, et al., “Electrostatic moire potential from twisted-hBN layers”, Nature Materials, 23, 65 (2024). DOI: 10.1038/s41563-023-01637-7

Exascale Catalytic Chemistry (ECC) Project

Lead Investigator: Judit Zádor, jzador@sandia.gov
Participating Institutions: Sandia National Laboratories, Argonne National Laboratory, Pacific Northwest National Laboratory, Brown University, Northeastern University
Source of Support: DOE-BES CTC, part of the Computational Chemical Sciences group
Website: https://www.ecc-project.org/
Keywords: heterogeneous catalysis; automated workflows; plane-wave DFT; microkinetic models; kinetic Monte Carlo; anharmonic partition functions

Project Scope

The goal of the ECC Project is to build predictive models for gas/solid heterogeneous catalytic systems using approaches shown in Fig. 1. In ECC we want to go beyond many of the approximations routinely used in simulating such systems and:

- Improve the accuracy of enthalpic as well as entropic contributions in thermodynamic functions of adsorbates at minima and first-order saddle points.
- Advance the state of the art in modeling the kinetics of catalytic reaction systems by creating automated frameworks with more realistic physical representations.
- Create and extend exascale-ready computational tools that can achieve our scientific goals and help others to adopt our approaches.

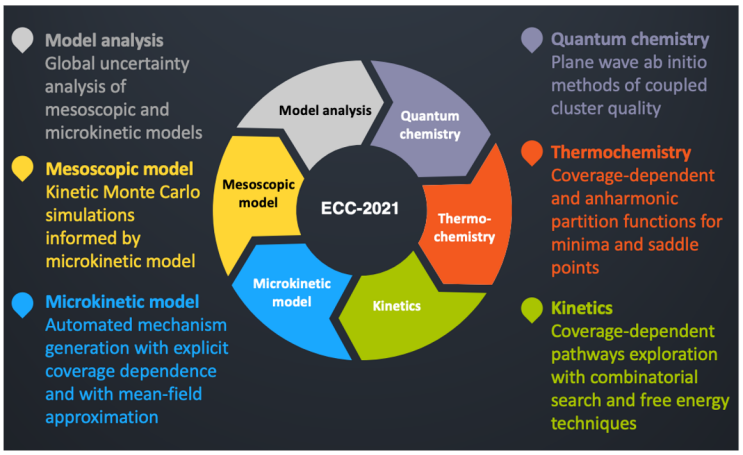


Figure 1. The ECC Project brings together a comprehensive set of computational tools to build predictive models for heterogeneous catalysis in an efficient, automated, accurate, and exascale-ready manner.

Technical Progress

We have developed the NWChemEx plane-wave DFT method (PWDFT) using a hybrid OpenMP-GPU framework, utilizing SYCL, OpenCL, and CUDA GPU kernels, in collaboration with the Argonne Leadership Computing Facility (ALCF) and Intel, through ECC's INCITE Science Proposal. We also derived our extension of correlation optimized virtual orbitals, COVOs for periodic systems, and we have been able to develop straightforward procedures for the second-quantization integrals for a full CI calculation.

To improve thermochemical predictions, we developed an importance-sampling integration approach that relies on truncated Gaussian mixture weights informed by potential energy surface minima and their corresponding Hessians. Additionally, we developed a new method for improving the accuracy of enthalpies of formation for adsorbates via homodesmotic reactions.

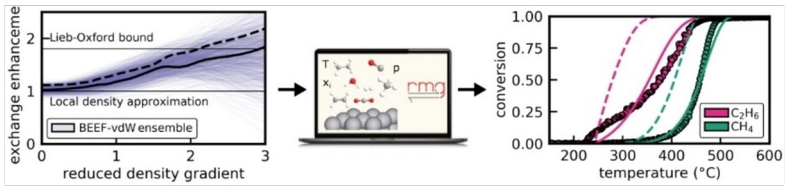


Figure 2. Automated generation of microkinetics for heterogeneously catalyzed reactions considering correlated uncertainties.

We demonstrated our automated workflow, Pynta, to explore reactions on surfaces and the code is currently used in a number of application projects. We implemented a low-data machine-learning approach to improve saddle point guesses in Pynta and a novel approach to directly investigate lateral interactions. We also developed a new theoretical framework for

diffusion-controlled chemical kinetic systems, and extended our optimizer, Sella.

We have published a study using the Blowers-Masel approximation to improve kinetics estimates in Reaction Mechanism Generator (RMG), and used uncertainty quantification (UQ) and Bayesian parameter estimation to study the microkinetic models of MeOH synthesis. We have added a representation of coverage-dependent thermochemistry to RMG and developed a workflow for calculating coverage-dependent adsorption energies. Additionally, we studied correlated uncertainties in the generated microkinetic mechanisms (see Fig. 2), and included bidentate species in RMG.

We have developed KinCat, an open-source two-dimensional lattice-based kinetic Monte Carlo (KMC) simulation software using C++ and the Kokkos library, intended for use in catalysis research. KinCat can run on a wide-variety of shared-memory architectures, including OpenMP and CUDA. It utilizes sophisticated pre-processing taking advantage of symmetry, shared memory to run with multiple compute threads without delays from message-passing between nodes, and HDF5 functionality for efficient standardized I/O.

We developed and demonstrated a polynomial chaos (PC) based approach that jointly represents both intrinsic and parametric uncertainties. We also generalized the method, via Karhunen-Loève expansions, to capture spatio-temporal stochastic fields and leveraged closed-form solutions for PC-based sensitivity indices to quantify the contributions of intrinsic noise to the overall variance of the model output. We have improved a means to estimate and report correlated uncertainties in the kinetic parameters of models generated by RMG.

Future Plans

We will fully integrate PWDT with the Pynta workflow. We will also explore the use of high-level many-body calculations, commonly used in quantum chemistry, such as Full Configuration Interaction (FCI) and Coupled Cluster (CC) approaches based on the periodic COVOs and COVOS-QFLOW methods.

We will use the importance sampling method developed in the last period to generate a reasonable number of samples to test concentration dependence and compare our methods to experimental thermochemistry as we gain access to Aurora during its early science phase. We will target cobalt systems important in Fischer-Tropsch.

Building on the current lateral interaction work, we plan to implement an active-learning approach to improve accuracy. Besides applications (methanol/Ag, organo-lithium, ammonia/Pt), we are preparing our code for the upcoming INCITE allocation.

We will work on a new functionality in RMG to recognize resonance structures for adsorbed species and to handle adsorbates that contain nitrogen, and analyze bimolecular reactions on surfaces, particularly reactions involving the transfer of H atoms from one adsorbate to another.

We will convert the KinCat preprocessor from the current Python implementation to C++, which will enable handling of more complex chemical systems. We will also apply KinCat's functionality to complex ammonia synthesis and decomposition models.

We will extend the parametrized stochastic surrogate construction to incorporate information from KMC simulations of different lattice sizes, employing multifidelity UQ methods. We will also implement a Bayesian procedure for specifying uncertain jointly correlated forward and reverse rates as input to KinCat. We also plan to link the RMG-generated parameter uncertainties to the SNL UQ code.

Broader Impacts and Workforce Development

We train undergraduates, graduates, and postdocs, and held training for our codes at the Fall ACS Meeting.

Data Management and Open Access

- RMG, https://github.com/ReactionMechanismGenerator/RMG-Py
- KinCat https://github.com/sandialabs/kincat
- Pynta https://github.com/zadorlab/pynta
- Sella https://github.com/zadorlab/sella
- PySIDT https://github.com/zadorlab/PySIDT
- NWChemEX PWDFT https://github.com/ebylaska/PWDFT, https://github.com/NWChemEx-Project
- AdTherm https://github.com/franklingoldsmith/adtherm

Publications and References

1. K. Blöndal, K. Badger, K. Sargsyan, D. H. Bross, B. Ruscic and C. F. Goldsmith, *Importance sampling within configuration space integration for adsorbate thermophysical properties: a case study for CH3/Ni(111)*, Physical Chemistry Chemical Physics **26**, 17265-17273 (2024). 10.1039/D4CP01197J
2. C. Xu, E. J. Mazeau and R. H. West, *Implementing the Blowers–Masel Approximation to Scale Activation Energy Based on Reaction Enthalpy in Mean-Field Microkinetic Modeling for Catalytic Methane Partial Oxidation*, ACS Catalysis **14**, 8013-8029 (2024). 10.1021/acscatal.3c05436
3. M. S. Johnson, J. N. Mueller, C. Daniels, H. N. Najm and J. Zádor, *Diffusion-Limited Kinetics in Reactive Systems*, The Journal of Physical Chemistry A **128**, 3685-3702 (2024). 10.1021/acs.jpca.4c00727
4. N. A. Hansen, T. D. Price, L. R. Filardi, S. M. Gurses, W. Zhou, N. Hansen, D. L. Osborn, J. Zádor and C. X. Kronawitter, *The photoionization of methoxymethanol: Fingerprinting a reactive C2 oxygenate in a complex reactive mixture*, The Journal of Chemical Physics **160**, (2024). 10.1063/5.0197827
5. B. Kreitz, K. Blöndal, K. Badger, R. H. West and C. F. Goldsmith, *Automatic mechanism generation involving kinetics of surface reactions with bidentate adsorbates*, Digital Discovery **3**, 173-185 (2024). 10.1039/D3DD00184A
6. B. Kreitz, P. Lott, F. Studt, A. J. Medford, O. Deutschmann and C. F. Goldsmith, *Automated Generation of Microkinetics for Heterogeneously Catalyzed Reactions Considering Correlated Uncertainties***, Angewandte Chemie International Edition **62**, e202306514 (2023). https://doi.org/10.1002/anie.202306514
7. M. S. Johnson, M. Gierada, E. D. Hermes, D. H. Bross, K. Sargsyan, H. N. Najm and J. Zádor, *Pynta—An Automated Workflow for Calculation of Surface and Gas‑Surface Kinetics*, Journal of Chemical Information and Modeling **63**, 5153-5168 (2023). 10.1021/acs.jcim.3c00948
8. B. Kreitz, G. D. Wehinger, C. F. Goldsmith and T. Turek, *Microkinetic Modeling of the Transient CO2 Methanation with DFT-Based Uncertainties in a Berty Reactor*, ChemCatChem **14**, e202200570 (2022). https://doi.org/10.1002/cctc.202200570
9. D. Song, N. P. Bauman, G. Prawiroatmodjo, B. Peng, C. Granade, K. M. Rosso, G. H. Low, M. Roetteler, K. Kowalski and E. J. Bylaska, *Periodic plane-wave electronic structure calculations on quantum computers*, Materials Theory **7**, 2 (2023). 10.1186/s41313-022-00049-5
10. K. Blöndal, K. Sargsyan, D. H. Bross, B. Ruscic and C. F. Goldsmith, *Configuration Space Integration for Adsorbate Partition Functions: The Effect of Anharmonicity on the Thermophysical Properties of CO–Pt(111) and CH3OH–Cu(111)*, ACS Catalysis **13**, 19-32 (2023). 10.1021/acscatal.2c04246
11. J. P. Perdew, S. T. u. R. Chowdhury, C. Shahi, A. D. Kaplan, D. Song and E. J. Bylaska, *Symmetry Breaking with the SCAN Density Functional Describes Strong Correlation in the Singlet Carbon Dimer*, The Journal of Physical Chemistry A **127**, 384-389 (2023). 10.1021/acs.jpca.2c07590
12. M. S. Johnson, X. Dong, A. Grinberg Dana, Y. Chung, D. Farina, Jr., R. J. Gillis, M. Liu, N. W. Yee, K. Blondal, E. Mazeau, C. A. Grambow, A. M. Payne, K. A. Spiekermann, H.-W. Pang, C. F. Goldsmith, R. H. West and W. H. Green, *RMG Database for Chemical Property Prediction*, Journal of Chemical Information and Modeling **62**, 4906-4915 (2022). 13.1021/acs.jcim.2c00965
14. E. D. Hermes, K. Sargsyan, H. N. Najm and J. Zádor, *Sella, an Open-Source Automation-Friendly Molecular Saddle Point Optimizer*, Journal of Chemical Theory and Computation **18**, 6974-6988 (2022). 10.1021/acs.jctc.2c00395
15. G. D. Wehinger, B. Kreitz and C. F. Goldsmith, *Non-Idealities in Lab-Scale Kinetic Testing: A Theoretical Study of a Modular Temkin Reactor*, Catalysts **12**, 349 (2022).
16. B. Kreitz, P. Lott, J. Bae, K. Blöndal, S. Angeli, Z. W. Ulissi, F. Studt, C. F. Goldsmith and O. Deutschmann, *Detailed Microkinetics for the Oxidation of Exhaust Gas Emissions through Automated Mechanism Generation*, ACS Catalysis **12**, 11137-11151 (2022). 10.1021/acscatal.2c03378
17. E. J. Bylaska, D. Song, E. S. Ilton, S. O'Leary, T. L. Torralba-Sánchez and P. G. Tratnyek, *Chapter Five - Building toward the future in chemical and materials simulation with accessible and intelligently designed web applications*, in Annual Reports in Computational Chemistry, ed. D. A. Dixon, Elsevier (2021), vol. 17, pp. 163-208.
18. M. Liu, A. Grinberg Dana, M. S. Johnson, M. J. Goldman, A. Jocher, A. M., C. A. Grambow, K. Han, N. W. Yee, E. J. Mazeau, K. Blondal, R. H. West, C. F. Goldsmith and W. H. Green, *Reaction Mechanism Generator v3.0: Advances in Automatic Mechanism Generation*, Journal of Chemical Information and Modeling **61**, 2686-2696 (2021). 10.1021/acs.jcim.0c01480
19. B. Ruscic and D. H. Bross, *Active Thermochemical Tables: the thermophysical and thermochemical properties of ethyl, CH3, and methylene, CH2, corrected for nonrigid rotor and anharmonic oscillator effects*, Molecular Physics **119**, e1969046 (2021). 10.1080/00268976.2021.1969046
20. K. Blöndal, K. Sargsyan, D. H. Bross, B. Ruscic and C. F. Goldsmith, *Adsorbate Partition Functions via Phase Space Integration: Quantifying the Effect of Translational Anharmonicity on Thermodynamic Properties*, The Journal of Physical Chemistry C **125**, 20249-20260 (2021). 10.1021/acs.jpcc.1c04009

Inverse Designing Metamaterials with Programmable Nonlinear Functional Responses in Graph Space

Lead Investigator: Xiaoyu (Rayne) Zheng, rayne23@berkeley.edu
Participating Institutions: Department of Materials Science and Engineering, University of California Berkeley. Graduate Program in Acoustics, Penn State University.
Department of Computer Science, University of California Los Angeles.
Department of Civil and Environmental Engineering, University of California Los Angeles.
Source of Support: NSF-DMREF
Website: none
Keywords: Metamaterials, Graph Neural Networks, Inverse Design, Deep Learning, Nonlinear Responses

Project Scope

This project aims to develop a graph-based machine learning framework, GraphMetaMat, for inverse designing metamaterials with programmable nonlinear functional responses (see Figure 1). Three-dimensional (3D) truss metamaterials with prescribed quasi-static stress-strain and viscoelastic transmissibility curves are demonstrated as proofs of concept. GraphMetaMat employs graph neural networks (GNN), deep imitation learning (IL), reinforcement learning (RL), and Monte Carlo tree search (MCTS) to generate metamaterial designs. We showcase its versatility with real-world applications, including chest protectors for sports (1) and vibration damping panels for electric vehicles (EVs) (2).

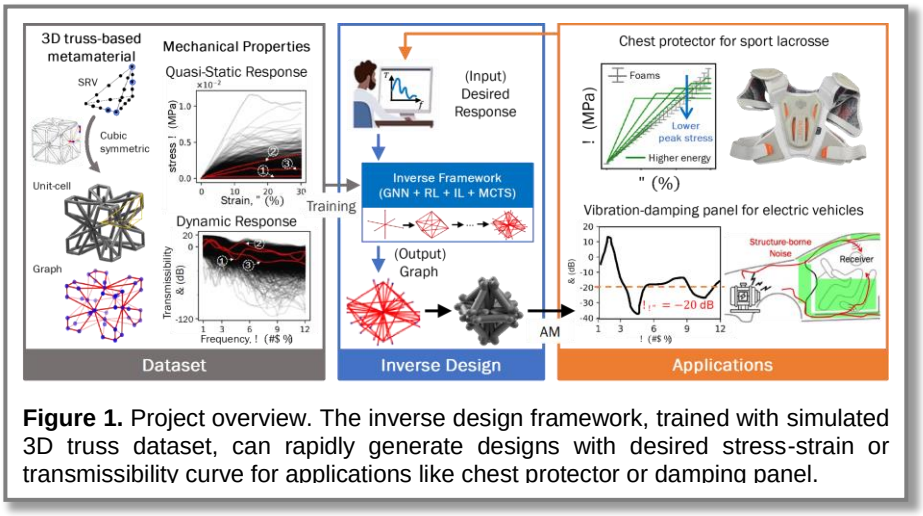


Figure 1. Project overview. The inverse design framework, trained with simulated 3D truss dataset, can rapidly generate designs with desired stress-strain or transmissibility curve for applications like chest protector or damping panel.

Relevance to MGI

To harness the power of data, this project employs graph representation as a computationally interpretable data structure for 3D truss metamaterials. This approach is more efficient as it inherently captures the structural information of truss topologies. Building upon this foundation, GraphMetaMat transforms a vast and discrete truss design space into a unified, continuous latent space (3). Mechanical properties of each structure are collected through finite element (FE) simulations with material properties characterized by experimental data, ensuring high-fidelity dataset for training. Enable by additive manufacturing, the generated designs from proposed GraphMetaMat are 3D-printed for compression and vibration tests to validate the proposed framework. Overall, this project achieves tight integration of computation, theory and experiment through a closed, iterative feedback loop to improve each component and enhance project outcomes. The proposed framework significantly accelerates the design process compared to traditional methods, aligning with MGI's goal of discovering new materials faster and at lower cost.

Technical Progress

Here we report the major achievements that have been accomplished during the past year. First, an efficient data-driven approach to translate any truss metamaterials into graphs for GNN-based design was developed, enabling us to exploit the inductive biases of GNNs (4). We emphasize that in principle our framework is not limited to truss metamaterials but any graph-representable metamaterials, paving the way for a unified metamaterial design framework. While existing approaches, often ML-driven, excel at efficiently optimizing specific properties (5–11), a key challenge in the design of architected materials remains in the inability to capture complex, on-demand functionalities (12). To face this challenge, we established an inverse-design framework, *GraphMetaMat*, to design

complex 3D truss metamaterials with nonlinear programmable functional responses. The framework is based on GNNs, deep imitation learning (IL), reinforcement learning (RL), and Monte Carlo tree search (MCTS). A GNN-based forward model is first trained to serve as response predictor given a metamaterial structure (represented as a graph). To improve the model generalization capabilities, physics biases and pre-training were adopted, reaching an accuracy of ~ 90 % with only 3000 labeled data. Inverse design is performed by an autoregressive GNN-based policy network, which predicts a sequence of actions needed to construct a graph given a desired physical response. IL and RL are employed to train the policy network, while MCTS to improve model accuracy at inference. During RL, the forward model is utilized to evaluate the generated graph's response, acting as a surrogate model.

As impactful proofs of concept, GraphMetaMat was tested on quasi-static compression stress-strain and viscoelastic transmission responses. Stiffness, strength, energy absorption, and vibration damping, are all information inherently brought by these two mechanical responses, hence, representing material's characteristic fingerprints. Using calibrated high fidelity FE simulations, two labeled datasets with ~ 3000 graph-curve pairs were collected and used to train and test our framework. While performance of the forward and inverse model was evaluated using part of these data, we also challenged our framework on the inverse design of user-defined curves where the existence of an associated structure is not a-priori guaranteed. To this scope, we not only designed stress-strain and wave transmission response types that extend beyond the dataset response space but also applied GraphMetaMat to design a chest protector's cushioning material and a vibration-damping panel for EVs. Although forward model's generalization capabilities represent a big challenge worth of future research, our framework could surprisingly rapidly design lightweight metamaterials with high energy absorption yet low peak stress for protective equipment and with low transmission for vibration-damping panels in EVs.

Future Plans

While truss metamaterials are selected as proofs of concept, the proposed framework can handle any graph-representable metamaterial. This versatility also extends to various physical responses, not limited to the showcased stress-strain and transmissibility curves. Future work includes using larger unified datasets and extending GraphMetaMat to design multiple responses simultaneously, enabling rapid, automatic design of multi-functional metamaterials.

Broader Impacts and Workforce Development

The proposed framework significantly advances materials science and engineering by introducing a novel approach to metamaterial design, aligning with the MGI philosophy. Its ability to rapidly generate tailored metamaterial designs can accelerate innovation across industries like automotive, aerospace, and personal protective equipment. From an educational perspective, this project provides a platform for training future materials scientists and engineers in cutting-edge ML algorithms, FE simulation, and AM for materials design. The project's interdisciplinary nature fosters collaboration and skill development in materials science, computer science, and physics. Our results will be disseminated through publications, conferences, and industry collaborations, meeting the evolving needs of the R&D workforce.

Data Management and Open Access

Research results have been disseminated through joint publications in peer-reviewed journals (including one in open access) and conference presentations. All publications are hosted on eScholarship—UCLA's open-access institutional repository. All simulation and machine learning codes as well as collected computational and experimental datasets have been/will be made available on shared GitHub repositories and Google Drive folders (DOIs upon official papers publication), in accordance with the MGI Strategic Plan. Videos of lectures, short-course, and conference presentations have been shared on the YouTube channel by all PIs.

Advancing Along the Materials Development Continuum and Partnerships to Translation

GraphMetaMat accelerates materials discovery by enabling rapid, automated design of metamaterials with tailored properties. As evidenced by two showcased applications, we highlight the framework's ability to translate fundamental research into practical innovations across industries like automotive, aerospace, and personal protective equipment. To facilitate technology transfer from fundamental research, we aim to implement open-access dataset, codes and lectures (See Data Management and Open Access). We are actively seeking partnerships with industry and evaluating potential patent to apply our proposed GraphMetaMat in real-world applications, paving the way for broader adoption of this technology.

Publications and References

1. E. I. Drewniak, D. B. Spenciner, and J. J. Crisco. Mechanical properties of chest protectors and the likelihood of ventricular fibrillation due to commotio cordis. Journal of Applied Biomechanics 23, (2007). doi:10.1123/jab.23.4.282

2. B. Meek, H. Van Der Auwear, and K. De Langhe. Challenges in NVH for electric vehicles. in Lecture Notes in Electrical Engineering 191 LNEE, (2013). doi:10.1007/978-3-642-33777-2_56

3. L. Zheng, K. Karapiperis, S. Kumar, and D. M. Kochmann. Unifying the design space and optimizing linear and nonlinear truss metamaterials by generative modeling. Nature Communications 14, (2023). doi:10.1038/s41467-023-42068-x

4. K. Xu, S. Jegelka, W. Hu, and J. Leskovec. How powerful are graph neural networks? in 7th International Conference on Learning Representations, ICLR 2019 (2019).

5. J.-H. Bastek, S. Kumar, B. Telgen, R. N. Glaesener, and D. M. Kochmann. Inverting the structure–property map of truss metamaterials by deep learning. Proceedings of the National Academy of Sciences 119, e2111505119 (2022). doi:10.1073/pnas.2111505119

6. S. Luan, E. Chen, J. John, and S. Gaitanaros. A data-driven framework for structure-property correlation in ordered and disordered cellular metamaterials. Science Advances 9, (2023). doi:10.1126/sciadv.adi1453

7. Y. Mao, Q. He, and X. Zhao. Designing complex architectured materials with generative adversarial networks. Science Advances 6, eaaz4169 (2020). doi:10.1126/sciadv.aaz4169

8. S. Kumar, S. Tan, L. Zheng, and D. M. Kochmann. Inverse-designed spinodoid metamaterials. npj Computational Materials 6, 1–10 (2020). doi:10.1038/s41524-020-0341-6

9. L. Zheng, S. Kumar, and D. M. Kochmann. Data-driven topology optimization of spinodoid metamaterials with seamlessly tunable anisotropy. Computer Methods in Applied Mechanics and Engineering 383, (2021). doi:10.1016/j.cma.2021.113894

10. S. Van ’t Sant, P. Thakolkaran, J. Martínez, and S. Kumar. Inverse-designed growth-based cellular metamaterials. Mechanics of Materials 182, (2023). doi:10.1016/j.mechmat.2023.104668

11. S. C. Shen and M. J. Buehler. Nature-inspired architected materials using unsupervised deep learning. Communications Engineering 1, (2022). doi:10.1038/s44172-022-00037-0

12. X. Zheng, X. Zhang, T. Te Chen, and I. Watanabe. Deep Learning in Mechanical Metamaterials: From Prediction and Generation to Inverse Design. Advanced Materials 35, Preprint at https://doi.org/10.1002/adma.202302530 (2023) doi:10.1002/adma.202302530

From Wavefunctions to Exchange Correlation for Large-scale Electronic Structure Calculations

Lead Investigator: Paul Zimmerman, paulzim@umich.edu.
Participating Institutions: University of Michigan, Ann Arbor
Website: None.
Keywords: Configuration Interaction, Inverse DFT, Data-driven exchange correlation approximation, Wavefunction theory, Density functional theory

Project Scope

This project seeks to increase the accuracy and application scope of wave function theory (WFT) and density function theory (DFT) electronic methods through new scalable, highly accurate computational algorithms, and data-driven approaches. To provide a step function increase in DFT accuracy, density inversion will map the full configuration interaction (FCI) electron density to the exchange-correlation potential, which is the quantum mechanical component of DFT. Alongside the use of WFT to create precise electron densities, this development will allow training of new density functionals to reproduce the exact 3D exchange-correlation potential. The new functionals—constructed via system identification and machine learning through deep neural networks—will push DFT towards the ability to capture strong correlation, with the goal of achieving WFT-like accuracy.

Relevance to MGI

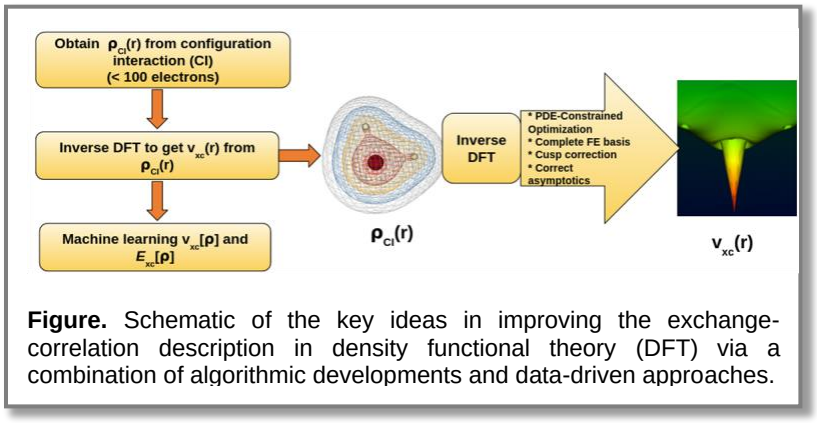


Figure. Schematic of the key ideas in improving the exchange-correlation description in density functional theory (DFT) via a combination of algorithmic developments and data-driven approaches.

The proposed work uses the integration of recent advances in the algorithms, scalable implementations on HPC architectures and data-driven approaches to improve the exchange-correlation description in density functional theory. In particular, we use incremental full configuration interaction (iFCI) calculation to compute accurate ground-state densities and energies on polyatomic molecules, and subsequently compute the exchange correlation (XC) potential corresponding to these ab-initio correlated densities via recent advances in the solution of the inverse DFT problem. We use the data on the exact XC potentials to not only evaluate the existing XC functional models, but also use data-driven approaches to improve the XC functional description. We anticipate that these developments will enable accurate electronic structure calculations using density functional theory for materials systems with both weak and strong correlations, and thus accelerate our understanding of materials behavior and materials discovery.

Technical Progress

In this project, we have advanced the algorithms and implementation of configuration interaction calculations on parallel computing architectures. This includes advances in parallel heat bath configuration interaction calculations [1] as well as development of methods to use Slater basis in configuration interaction calculations [2]—crucial to compute accurate densities with correct asymptotics. We have extended our inverse DFT formalism using PDE constrained optimization solved in a finite-element basis [3] to spin polarized (open shell) systems [4], and we are generating the exact XC potentials from ab-initio correlation electron densities for both closed shell and open shell systems obtained from accurate iFCI calculations. We have used these exact XC potentials to evaluate the accuracy of model DFT XC functionals and identified $O(10^{-1} – 10^{0})$ relative errors in many metrics involving model

XC potentials [5,4]. We have also leveraged the ability of accurately solving the inverse DFT problem to assess density and functional dependent errors for various model XC functionals [6-7]. We have also achieved algorithmic and HPC advances for fast and accurate evaluation of XC potentials from ground-state densities [8-9]. We presently have the data on a range of atomic and molecular systems and are continuing to generate more data. Further, we have developed the framework to use the data on the ground-state densities, energies, and the corresponding exact XC potentials to develop better XC models using machine-learning ideas [8]. To this end, we have created a neural network (NN) based local spin density approximation (NN-LDA) and a neural network based generalized gradient approximation (NN-GGA), utilizing the exact XC potentials from our inverse DFT calculations. Using the data on only a few systems (Li, N, Ne, H_2 and LiH), the NN-LDA and NN-GGA models shows substantially improved accuracy in the ground-state energies. In particular, the mean absolute error for the ground-state energies on the G2 dataset for the NN-GGA is ~2kCal/mol, which is substantially lower than widely used DFT functionals. The model also provides good improvements in atomization energies and reaction barriers. We have also developed additional NN based models for Laplacian level meta-GGA functional and those based on fractional derivatives, which are presently being evaluated. We have also integrated the developed functionals into the DFT-FE code [10-11] and demonstrated calculations at scale on many hybrid computing architectures [8].

Future Plans

In the next year of this project, we will continue generating exact XC potentials for a wider range of molecules to augment the training data for our NN based XC models. Additionally, we will evaluate and continue the development of more expressive XC models at the level of meta-GGA and generalized gradient approximation (GDA), which will include both integral and fractional derivatives of the density. For each of the models, we will extensively benchmark their accuracy against thermochemical datasets. Further, we will release the code for inversion DFT calculations (GPU ported) and the library of XC potentials computed in this work.

Broader Impacts and Workforce Development

The junior researchers on this project are being trained by the PIs on a variety of aspects of scientific computation, ranging from theoretical and mathematical aspects of electronic structure to good programming practices and parallel computing. The project outcomes are being shared with the broader community via open-source codes and data-sharing, besides publications and presentations at meetings.

Data Management and Open Access

The open-source aspect is a big part of this project, where the developed codes, the data obtained on the XC potentials, and the developed XC models will all be made public over the course of the project. Some aspects of the codes are already open source: (a) SlaterGPU library (https://github.com/ZimmermanGroup/SlaterGPU); (b) DFT-FE codebase (https://github.com/dftfeDevelopers/dftfe) over which the public version of inverse DFT algorithm will be made available.

Advancing Along the Materials Development Continuum and Partnerships to Translation

We anticipate that the data on the exact XC potentials will substantially accelerate the development of new XC functionals with increasing accuracy for both weakly- and strongly-correlated systems. Thus, this effort will overall improve the accuracy of DFT calculations, which is the workhorse of electronic structure calculations in MGI. These developments coupled with the advances towards scalable large-scale DFT calculations on exascale computing architectures has the significant potential of accelerating materials discovery.

Publications and References

1. Dang, D.-K., Kammeraad, J.A., Zimmerman, P.M., Advances in parallel heat bath configuration interaction, *J. Phys. Chem. A* 127, 400 (2023).
2. Dang, D.-K., Wilson, L.W., Zimmerman, P.M., The numerical evaluation of slater integrals on graphics processing units, *J. Comput. Chem.* 43, 1680 (2022).
3. Kanungo, B., Zimmerman, P., Gavini, V., Exact exchange-correlation potentials from ground-state electron densities, *Nature Communications* 10, 4497 (2019).
4. Kanungo, B., Hatch, J., Zimmerman, P., Gavini, V., Exact and model exchange-correlation potentials for open-shell systems, *J. Phys. Chem. Lett.* 14,10039-10045 (2023).
5. Kanungo, B., Zimmerman, P., Gavini, V., A comparison of exact and model exchange-correlation potentials for molecules, *J. Phys. Chem. Lett.* 12, 12012-12019 (2021).
6. Kanungo, B., Kaplan, A.D., Shahi, C., Gavini, V., Perdew, J.P., Unconventional error cancellation explains the success of Hartree-Fock density functional theory for barrier heights, *J. Phys. Chem. Lett.* 15, 323-328 (2024).
7. Kaplan, A.D., Shahi, C., Sah, R., Bhetwal, P., Kanungo, B., Gavini, V., Perdew, J.P., How does HF-DFT achieve chemical accuracy for water clusters?, *J. Chem. Theory Comput.* to appear (2024), DOI: 10.1021/acs.jctc.4c00560.
8. Das, S., Kanungo, B., Subramanian, V., Panigrahi, G., Motamarri, P., Rogers, D.M., Zimmerman, P., Gavini, V., Large-scale materials modeling at quantum accuracy: Ab initio simulations of quasicrystals and interacting extended defects in metallic alloys, *Proceedings of SC23, The International Conference for High Performance Computing, Networking, Storage, and Analysis*, Article No. 1 (2023). [2023 ACM Gordon Bell Prize]
9. Tribedi, S., Dang, D.-K., Kanungo, B., Gavini, V., Zimmerman, P., Exchange correlation potentials from full configuration interaction in a Slater orbital basis, *J. Chem. Phys.* 159, 054106 (2023).
10. Motamarri, P., Das, S., Rudraraju, S., Ghosh, K., Davydov, D., Gavini, V., DFT-FE: A massively parallel adaptive finite-element code for large-scale density functional theory calculations, *Comput. Phys. Commun.* 246, 106853 (2020).
11. Das, S., Motamarri, P., Subramanian, V., Rogers, D.M., Gavini, V., DFT-FE 1.0: A massively parallel hybrid CPU-GPU density functional theory code using finite-element discretization, *Comput. Phys. Commun.* 280, 108473 (2022).