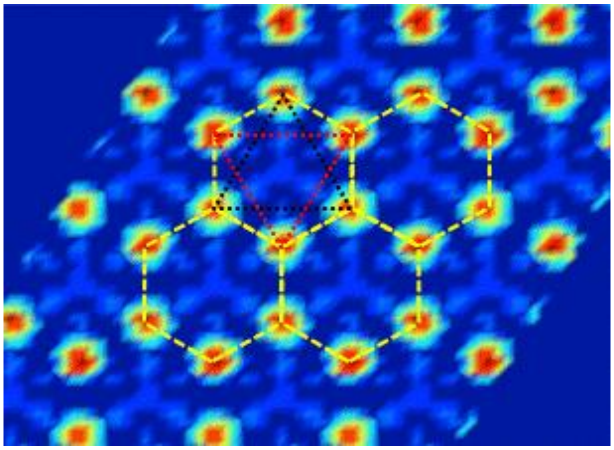
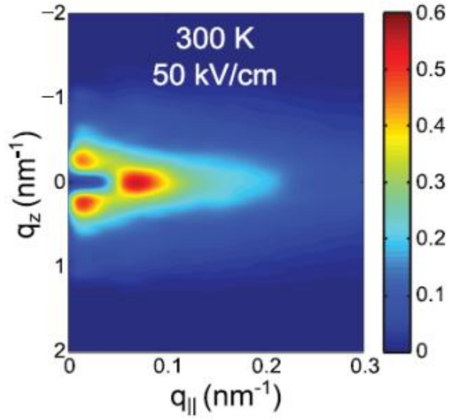
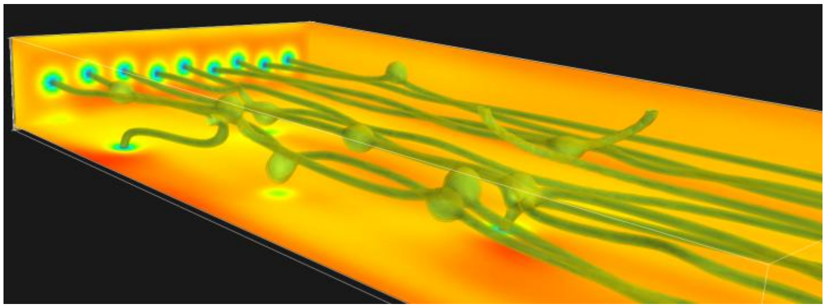
# DOE/NSF Materials Genome Initiative

## 2nd Annual Principal Investigator Meeting

## Accelerating Materials Research, Meeting Societal Needs, Building Infrastructure for Success







Bethesda, MD

12–13 January 2015

# On the Cover

Top: Electron density at the interface of a $LaAlO_3/SrTiO_3$ epitaxial heterostructure, showing Graphene-like honeycomb coordination. Figure is a two-dimensional slice of the three-dimensional charge density obtained by Coherent Bragg Analysis (COBRA) measurements at the Advanced Photon Source. Chang-Beom Eom, University of Wisconsin, unpublished.

Lower Left: Non-equilibrium phonon distribution in mid-infrared quantum cascade laser. Y. B. Shi and I. Knezevic, J. Applied Physics, **116**, 123105 (2014).

Lower Right: Illustration of vortex state for rectangular superconductor in a parallel magnetic field determined from numerical solution of time dependent Ginzberg-Landau equations. Andreas Glatz, Argonne National Laboratory, Unpublished.

# Foreword

This volume provides descriptions of projects presented at a joint DOE/NSF Materials Genome Initiative (MGI) Principal Investigator's Meeting held January 12-13, 2015, in Bethesda, Maryland.

The Materials Genome Initiative (MGI) is an interagency program intended to shorten the time to bring new materials from discovery to deployment. It combines computational tools, experimental tools, and digital data in an iterative fashion leading to validated software, curated data, and materials synthesis. Further information on MGI is available at www.whitehouse.gov/MGI including the MGI Strategic Plan released in December 2014.

The meeting brought together principal investigators from NSF's DMREF Program (Designing Materials to Revolutionize and Engineer our Future) and the DOE's Predictive Theory and Modeling Program funded by the Office of Basic Energy Sciences (BES). Additional BES PIs were included from selected Energy Frontier Research Centers. The meeting provided a venue for scientists to present and exchange information about their research activities, to foster new ideas and establish collaborations, and to discuss future research directions. It also aided NSF/DOE in assessing the needs of this research community and in charting future programmatic directions.

Principal Investigators were asked to submit a two-page abstract and to prepare a poster. Several projects were selected for oral presentation; NSF and DOE program managers provided overviews of MGI and related research opportunities in their agencies.

DMREF supports activities that accelerate materials discovery and development by building the fundamental knowledge base needed to design and make materials with specific and desired functions or properties from first principles. This is accomplished by understanding the interrelationships of composition, structure, properties, processing, and performance. Achieving this goal will involve modeling, analysis, and simulation, validated through sample preparation, characterization, and device demonstration. It will require new data analytic tools and statistical algorithms; advanced simulations of material properties, advances in predictive modeling and a data infrastructure that is accessible, extensible, scalable, and sustainable.

BES supports fundamental research to understand, predict, and ultimately control matter and energy at the electronic, atomic, and molecular levels and fundamental research that provides the foundations for new energy technologies relevant to DOE's missions in energy, environment and national security. BES participants in the MGI have contributed fundamental advances in algorithms and codes, large public searchable databases, and applications to materials research in areas such as light alloys for transportation.

We thank all the meeting participants for their active contributions in sharing their ideas and research accomplishments. We wish to thank Teresa Crockett, BES, and Tammy Click and Verda Adkins-Ferber at the Oak Ridge Institute for Science and Education (ORISE) for their outstanding work in all aspects of the meeting organization.

Dr. James W. Davenport
Office of Basic Energy Sciences
US Department of Energy

Dr. John Schlueter
Division of Materials Research
National Science Foundation

# *Table of Contents*

# Table of Contents

## Breakout Session Reports

## Abstracts

# *Agenda*

# Agenda

**Monday, January 12**

8:00 Registration, Continental breakfast
8:30 **Mary Galvin** (NSF) & **Linda Horton** (DOE)
9:10 **Dane Morgan** (U. Wisconsin) 'Materials Accelerator Network'
9:40 **John Allison** (U. Michigan) 'Center for Predictive Integrated Structural Materials Science (PRISMS) – UM-DOE Software Innovation Center for the Structural Metals Community'
10:10 Refreshment break, poster setup
10:40 **Kristin Persson** (LBNL) 'The Materials Project for Accelerated Materials Design'
11:10 **Alex Zunger** (U. Colorado) 'Functionality-driven Discovery of Materials: Looking for Materials with Target Properties'
11:40 **Cyrus Wadia** (OSTP)
12:00 Breakout Session #1 with Working Lunch
*Challenges for Materials Classes*

1) Metals, Alloys & Structural Materials
   **Anton Van der Ven** (UC-Santa Barbara) & **Michael Demkowicz** (MIT)
2) Magnetic, Electronic, Superconducting & Photonic Materials
   **Karin Rabe** (Rutgers) & **Peter Johnson** (BNL)
3) Soft Materials: Polymers & Biomaterials
   **Pat Mather** (Syracuse) & **Edward Pyzer-Knapp** (Harvard)
4) Catalysis, Chemical Transformations & Energy Storage
   **Geoff Coates** (Cornell) & **Ilja Siepmann** (U. Minnesota)
5) Energy Materials: Photovoltaics, Thermoelectrics & Transport
   **Eric Toberer** (Colorado School of Mines) & **Neepa Maitra** (Hunter College)

13:30 Preparation of Reports
14:00 Presentation of Breakout Sessions (5 x 15 min)
15:15 Poster Session with Refreshments
17:00 Adjourn

**Tuesday, January 13**

8:00 Continental breakfast
8:30 Project presentations
  8:30 **John Parise** (SUNY – Stony Brook) 'High Pressure Synthesis of Novel Oxynitride Photocatalysis'
  8:40 **Tresa Pollock** (U. California – Santa Barbara) 'Discovery, Development, and Deployment of High Temperature Coating/Substrate Systems
  8:50 **Paul Kent** (ORNL) 'Network for *ab initio* Many-body Methods: Development, Education and Training'
  9:00 **Sinan Keten** (Northwestern) 'Simulation-based Design of Functional Sub-nanometer Porous Membranes'
  9:10 **Aravind Mohanram** (Saint-Gobain Ceramics and Plastics) 'Multi-scale Fundamental Investigation of Sintering Anisotropy'
  9:20 **Irena Knezevic** (U. Wisconsin) 'Coupling Electrons, Phonons, and Photons'
  9:30 **Sanjay Khare** (U. Toledo) 'Nitride Discovery - Creating the Knowledge Base for Hard Coatings'
  9:40 **Gregory Rutledge** (MIT) 'Computational and Experimental Discovery and Development of Additives for Novel Polymer Morphology and Performance'

9:50 **Sean Agnew** (U. Virginia) ‘Multi-scale Modeling and Characterization of Twinning-Induced Plasticity and Fracture in Magnesium Alloys’

10:00 **Aleksandra Vojvodic** (SLAC) ‘Predictive Theory of Transition Metal Oxide Catalysis’

10:10 **SonBinh Nguyen** (Northwestern) ‘A Fundamental Approach to Study the Effect of Structural and Chemical Composition in Functionalized Graphene Materials’

10:20 **Jihui Yang** (U. Washington) ‘High Efficiency Hierarchical Thermoelectric Composites by Multiscale Materials Design and Development’

10:30 Refreshment break

11:00 **Jim Warren** (NIST) ‘The MGI and Challenges in Materials Data’

11:30 Overview of Initiatives related to MGI (5 min each + 10 min Panel Discussion)

1) **Jim Davenport** (DOE) Computational Materials Science
2) **Sean Jones** (NSF) Materials Innovation Platforms
3) **Daryl Hess** (NSF) Scientific Software Innovation Institutes
4) **Anita Lasalle** (NSF) I-corps

12:00 Breakout Session #2 with Working Lunch

*Challenges for MGI*

1) Multiscale Computation & Modeling
   **Moneesh Upmanyu** (Northeastern) & **Efthimios Kaxiras** (Harvard)
2) Closing the Feedback Loop: Integrating Synthesis, Measurement & Computation
   **Janice Musfeldt** (Tennessee) & **David Sholl** (Georgia Tech)
3) Data: Depositories & Access
   **Tim Mueller** (Johns Hopkins) & **Thomas Proffen** (ORNL)
4) Equipping the Next Generation: Education, Training & Outreach
   **Hendrik Heinz** (Akron) & **Luke Shulenberger** (Sandia National Laboratory)
5) Community Codes & Open Source Software
   **James Lewis** (West Virginia) & **Francois Gygi** (U. California – Davis)

13:30 Preparation of Reports

14:00 Presentation of Breakout Sessions (5 x 15 min)

15:15 Poster Session with Refreshments

17:00 Adjourn

# *Breakout Session Reports*

# Metals, Alloys and Structural Materials

Moderators: M. J. Demkowicz (MIT), A. Van der Ven (UCSB)

This breakout session was attended by ~25 individuals. The format of the discussion involved going around the table and letting each attendee contribute his/her thoughts. AVDV took notes during the discussion. Many of the attendees provided additional input by directly emailing the moderators. This document provides a summary of all input received, following the format of the outbrief presentation given by MJD during the MGI PI meeting.

***What are structural materials?*** Alloys, but also ceramics, amorphous solids (such as metallic and oxide glasses), polymers and polymer composites.

***Design in structural materials.*** Structural materials are usually multi-functional and multi-component. Thus, designing structural materials is much more complex than targeting a single property, which might be cleanly linked to electronic structure. It requires accounting for the material's microstructure, defects (dislocations, grain boundaries, etc.), impurities, the environment, and the effect of non-zero (and possibly very high) temperatures.

***Interfaces.*** Interfaces play a crucial role in the processing and performance of structural materials. Thus, special attention must be given to them, even to the point of initiating an "interface genome" effort. Interfaces in structural materials include solid-state interfaces such as grain boundaries and heterophase interfaces (they govern mechanical properties, microstructure stability, etc.), electrochemical interfaces (which govern corrosion), solid-liquid interfaces (control processing through solidification), and interfaces formed by contacting bodies (which lead to friction and wear). Structure-property relations for all these classes of interfaces remain poorly understood, but are critical to materials design.

***Computation.*** In the field of structural materials, there are long-standing challenges that remain unresolved, such as fatigue, plasticity, and corrosion. To make progress on addressing these challenges, new theories and models are needed to connect atomic-level properties of structural materials to microstructure-scale behavior. Since such theories and models will be inherently multi-scale, ensuring their accuracy requires automatic error assessment and model fidelity selection.

***Characterization.*** Current methods of microstructure characterization are insufficient for the MGI. New descriptors that go beyond real space methods and better statistical sampling are required. Tools for microstructure analysis may be adapted from image processing, machine learning, or dimensionality reduction. Characterization should furthermore focus on finding ways to assess mechanisms of materials behavior, e.g. through increased reliance on *in situ* measurements.

***Processing and synthesis.*** Connecting materials design to processing remains a challenge—can we find ways to synthesize the materials that we design? Improved modeling of processing methods is also required. The challenges involved in modeling processing are similar to those in modeling materials behavior: processing is inherently multiscale. How do we bridge scales in processing and synthesis computations?

***Do not abandon systematic experimentation.*** MGI aims for materials by design. However, as we pursue this goal, we should not abandon traditional approaches of systematic experimentation. Such “tried-and-true” approaches have in the past led to surprising discoveries that theory/modeling could not have predicted, e.g. high-$T_c$ superconductors.

***Need for more theory and theorists.*** Theory—as opposed to modeling—is needed to connect properties of alloys and structural materials across scales to first-principles calculations. In particular, better meso-scale theories are required. A greater emphasis on statistical mechanics or formal model-order reduction may be of use.

***Workforce development.*** MGI requires software development, database curating, and other activities that are not presently incentivized and rewarded, e.g. in promotion processes. Ways of recognizing such contributions should be implemented. Since MGI involves many challenges related to data sciences, it is also important to involve people with technical backgrounds in computer science, electrical engineering, and others. Their expertise should begin to enter materials science curricula. Finally, for MGI to have an impact on industry, mechanisms for involving industry in MGI should be proposed.

# Magnetic, Electronic, Superconducting & Photonic Materials

Moderators: Peter Johnson (Brookhaven National Lab) and Karin Rabe (Rutgers)

There are many specific materials and functionality targets included in this broad class of materials. Interest is currently particularly high in rare-earth-free magnets, ferromagnetic ferroelectrics with strong coupling, materials for spintronics (especially ferromagnetic semiconductors), topological insulators, thermoelectrics and low thermal conductivity materials, n and p dopable semiconductors beyond silicon, field-controlled metal-insulator transitions, transparent conductors, lead-free piezoelectrics, piezoresistive materials, ionic conductors, high-$T_c$ superconductors, and materials with controlled optical properties for photonics and photoluminescent applications. The search for materials encompasses both known materials with previously unrecognized desirable properties and artificial structuring to achieve new systems in single crystals, superlattices and heteroestructures, and controlled microstructures.

Some specific challenges include identifying descriptors for complex functionalities such as ferroelectric switching fields and superconducting $T_c$, improving of experimental characterization techniques by better integration with first-principles capabilities, improving first-principles calculations for solids solutions and for strongly correlated materials, modeling and controlling the effects of defects on properties, achieving room temperature operation for a broad range of materials functionalities, and identification of materials that can be easily synthesized in very large quantities for certain large-scale applications, like the power grid.

The main focus of the discussion was on experimental-theoretical interaction. It was agreed that a cooperative approach, modeled on Bell Labs, in which one sample is studied by many investigators with complementary characterization techniques with prompt and interactive analysis by theory would be the ideal. The message here was that *experimentalists need to know which theoretical results to trust and theorists need to know which experimental results to trust.*

A further key issue is management of data, especially experimental data (first-principles data is under purview of Materials Project and related initiatives): collection, storage, analysis, verifying provenance and accessibility. This is particularly important for this class of materials discussed as there can be considerable variation from sample to sample, especially in the early stages of investigation.

With a roughly equal balance of experimentalists and theorists at the discussion, we asked each group to give a wish list to the other. Experimentalists would generally like to see more development of theoretical methods for certain properties. Examples being magnetoelectric coupling for noncollinear spin systems, defect-controlled properties, excited state properties of semiconductors, frequency dependent permittivity for optoelectronic applications, strongly correlated materials, and properties of materials away from equilibrium. Theorists would like to see a faster turnaround for synthesizing and characterizing new materials, currently on the scale of one to two years.

Two other themes emerged from the discussion. The first was an emphasis on the importance of models as a bridge between direct computation and experiment. The second was the striking of a balance between highly targeted investigations zeroing in on a particular materials goal, and “untargeted” investigations focusing on exploration of the fundamental physics of functional properties, which generate lots of varied candidates for promising materials. Both are necessary for rapid progress in materials discovery and design.

Finally, two specific recommendations were articulated. First, that a conference analogous to the current DMREF PI conference should be organized for students and postdocs, to leverage the energy, open thinking, and desire for interaction and collaboration among the junior participants in the DMREF program. Second, that the synergies between DMREF projects identified in the course of the workshop could be developed using internet technologies to foster Bell-Labs-style cooperation for collecting and analyzing materials data on high-quality shared samples.

Session Participants:
Tomo Uemura, David Vanderbilt, Eric Schwegler, Jan Musfeldt, Gang Cao, Dave Sellmyer, Jim Davenport, Peter Littlewood, Mary Galvin, Jim Horwitz, Jim Speck, Andy Schwartz, Ralph Wachter, Louis-Francois Arsenault, Lian Li, Haijan Wang, Aldo Romero, Steve White, Chuck Gartland, Volker Sorger, AJ Meir, Daniel Gall, Chang-Beom Eom, Mark Rzchowski, Mike Norman, Michael Weinert, Dimitris Perlidis, Avik Ghosh and Jim Eckstein

# Soft Materials: Polymers and Biomaterials

Moderators: Pat Mather (Syracuse) and Edward Pyzer-Knapp (Harvard)

In January of this year, a group of specialists in the areas of soft matter and biomaterials research met to contemplate the current status and future prospects for research in these fields with the construct of NSF's "Designing Materials to Revolutionize and Engineer our Future" (DMREF) program, part of the Materials Genome Initiative (MGI). Approximately twenty five (25) faculty and postdoctoral researchers across research areas ranging from polymer chemistry to multiscale modeling and peptide self-assembly asked each other to identify the challenges and opportunities for their fields, particularly within the paradigm of a DMREF research program, which intimately intertwines theory, experiment, and data. Prior to our discussion, it was understood that NSF's DMREF program receives comparatively fewer proposals than from the hard materials community, so one goal of the discussion was to speculate on why this is the case. The following briefly summarizes this discussion.

Soft Matter and Biomaterials research involves the study of a broad range of topics from elastomers to biomolecules and tissue engineering scaffolds that share in common their diversity of molecular architecture, complex nanostructure, and high deformability, to name just a few. Naturally, the group agreed, the complexity of soft matter research causes some broad challenges in systematically coupling experimental and theoretical research toward the generation of large datasets useful for materials discovery. Among the large challenges several broad themes emerged from the discussion. First, the data sets and materials descriptors associated with soft matter are large, complex, and involve metadata often taking the form of unparameterized observations. On the other hand, some newer materials systems have very little data accumulated for them. In addition, physical phenomena associated with soft materials often involve large deformations, complex interfaces, and long times, particularly hard to model. Collectively, identification of these broad themes led to consensus that there is a need for a central MGI platform for soft matter research.

The discussion continued with identification of several unique challenges for soft matter and biomaterials research that combines experiment and theory, summarized here. The dynamic behavior of such materials (responsive, adaptive, actuating, chemo-responsive) poses challenges to the development of intuition on how to design these materials. Moreover, while database searches associates with materials discovery seem to work well with hard materials, analogous searches are restricted to subsets of soft materials, particularly the simpler systems. It was further identified that, in contrast to hard materials, composition alone doesn't adequately specify unique structure and this is amplified by a strong influence of process on nanostructure and, for example, molecular orientation or nanofiller dispersion. Finally, soft matter and biomaterials are frequently not operating at their thermodynamic limits, which is especially problematic for systems of finite size.

Opportunities for Soft Matter and Biomaterials research within DMREF were also discussed. Significant interest was expressed for the study of responsive and adaptive materials, requiring improved understanding of the interaction of the materials with dynamic environments. In addition the non-equilibrium nature of soft matter was thought to expand the domain of possible properties, ripe for discovery of new phenomena for study and technological exploitation. Further, it was recognized that some large molecules assemble into prescribed shapes and sizes (e.g. globular proteins) for designed assembly, which may lend itself well to the DMREF paradigm for collaborative research.

The group wrapped up its discussion by identifying several salient points (take-home messages) for the NSF DMREF team and for the Soft Matter and Biomaterials communities. First, the need exists to develop an MGI platform specific to soft matter, embracing inherent features of multiscale and dynamic behavior and including metadata descriptors. Such a platform will look distinct from that of hard materials research for the reasons of complexity discussed earlier. Next, common materials descriptors, especially for micro- and nano-structure are needed for collective, coordinated research in these fields and the DMREF program is a good platform for developing them. Finally, the group strongly encourages other researchers from the Soft Matter and Biomaterials communities to engage with the MGI through the DMREF program by developing proposals that attempt to meet the challenges expressed above. It was felt that the benefits of collaboration among experimentalists, theorists, and computational scientists toward advancing our fields are well worth the effort.

# Catalysis, Chemical Transformations, and Energy Storage

Moderators: G. Coates (Cornell) and I. Siepmann (Minnesota)

Attendees:
J. Borreguero Calvo, A. Chaka, L. Gagliardi, J. Greeley, R. Hayes, M. Helm, H. Heinz, C. Henderson, M. Janik, T. Kaxiras, P. Kent, S. Klippenstein, P. Kroll, J. Lewis, D. Morgan, T. Mueller, S. Nguyen, J. Parise, M. Pederson, K. Persson, D. Sholl, B. Smit, R. Snurr, M. Toney, D. Vlachos, A. Vojvodic, and C. Wang

*Opportunities:*
This breakout group foresees significant opportunities in the area of hierarchical materials that include features at different length scales (also different state or composition, e.g., polymer-hard material composites, tandem reactions, multiple different catalytic sites) to exploit the synergy afforded by such materials; for example, microporosity and specific catalytic sites allow for selectivity (in catalysis and separations) and can be coupled with mesopores or control of nanocrystallinity to facilitate transport and increase turnover that are also important for facile delivery from energy (including gas) storage materials.

*Challenges:*
Similar challenges are faced by all the material functionalities considered by this breakout group and, in the interest of brevity, are discussed here in terms of heterogeneous catalytic materials:

- *in situ* characterization of all species and active reaction sites including characterization of defects and surface effects coupled iteratively with computation/theory to ensure that modeling can address the right system answers the right question;
- interplay of modeling/experiment/data is needed to understand synthesis and stability of materials; be able to address the kinetic and thermodynamic aspects of materials synthesis
- develop model systems that can capture the essential physics of real systems and can be varied systematically and characterize thoroughly including defects
- new computational methods and tools are needed for this more ‘realistic’ modeling, i.e., to predict the performance spread between batches of functional materials synthesized using the “same” protocol

*Recommendations:*

- Coordination within centers is often very good. How can we better coordinate across centers and different research groups?
- We need to maintain infrastructure over time scales longer than a PhD thesis
    - Funding already exists for hardware infrastructure
    - There is a need for analogous software efforts, as this community is generating enormous amounts of data, as well as new algorithms and codes, which should not evaporate at the end of a grant (University Libraries)
- Coordination of software infrastructure will avoid duplication of effort (but don’t stifle innovation)
- The materials community should discuss whether agreement on a data standard (e.g., PDB) would be beneficial?

# Energy Materials: Photovoltaics, Charge Transport, and Thermoelectrics

Moderators: Eric Toberer (Colorado School of Mines), Michael Chabinyc (UCSB),
and Neepa Maitra (New York University)

The development of high performance and cost-effective photovoltaics and thermoelectrics will greatly benefit from MGI-based approaches to accelerate discovery of new materials and processing methods. The MGI approach will improve our predictive capabilities to understand charge carrier scattering, electronic structure design, dopability, and the role of interfaces. This fundamental knowledge will widen the scope of available materials, improve their efficiencies and enable a more rapid transition to a renewable energy economy.

During the breakout session, we converged on several challenges where an MGI-based approach could lead to significant advances. These challenges span both hard and soft matter and include: (a) deepening our understanding of non-equilibrium charge transfer dynamics, (b) understanding the role of growth conditions, metastability, and reliability on materials properties and (c) developing predictive models for the impact of disorder, defects, and doping on majority and minority charge carrier transport.

The first opportunity is the theory, computation, and experimental realization of fully time-resolved studies of charge carrier dynamics in photovoltaic and thermoelectric applications. Both these applications are far from equilibrium and there is a need to develop reliable methods with a sense of error-estimates. Charge transport critically depends on lattice dynamics, or, ion dynamics generally, and as such, there is a need for coupled studies of charge carriers and atomic motion. Recent years have seen exciting work in this area, but the breakout session emphasized that more needs to be done to ensure the theory being used is on solid ground, to develop practical and user-friendly codes, and surmount the challenges of experimentally resolving the underlying carrier dynamics.

The second opportunity is to address metastability: many functional materials, e.g. thin films, are kinetically stable rather than thermodynamically stable in their highest performance form. This makes their synthesis difficult, and new design approaches are needed. Related is the question of reliability: the lifetime of the material is entangled with metastability and chemical reactivity with their environment. The breakout session highlighted computation's ability to map out the energy landscape for potentially deleterious reactions as an alternative to accelerated experimental testing.

The third opportunity is to develop design strategies for photovoltaics and thermoelectrics in disordered/defective hard and soft materials. Most theoretical models are based on translational symmetry that is broken in complex systems and at interfaces. For example, transport in the nanoscale morphology of complex organic blends is difficult to predict, and in crystalline semiconductors, defects and doping are critical determinants for transport properties. While in crystalline semiconductors the methods to predict energetics of point defects have seen significant advances in the last couple of decades, modeling of perturbations that defects introduce both on the static properties (e.g. on electronic structure) as well as on dynamics of solids (phonons, charge carrier scattering) remains a challenge. Phenomenological modeling may serve as a bridge between *ab initio* computation and experiment, especially for extrinsic defects.

Two common themes emerge from these opportunities. First, how accurate should computation be to accelerate our experimental realization of materials with desired properties? It is important to have a sense of the error estimate of the theory, at the same time bearing in mind that experiment is far from perfect. Second, how will we connect correlations within data with the underlying physics? Correlations between observables alone may accelerate discovery, but does not increase our physical understanding. If we can successfully unite material informatics with material physics, there is great potential for revolutionary materials and insight.

# Multiscale Computation & Modeling

Moderators: Moneesh Upmanyu (Northeastern) and Efthimios Kaxiras (Harvard)

The breakout session on multi-scale modeling identified four key issues: a) extending existing methodologies to experimentally relevant scales, b) key tools/paradigms that are missing and need development, c) cross-cutting universal ideas, and d) assessment of state of the art via tangible successful stories, if any, as opposed to hype/expectations.

All materials modeling efforts do not necessarily require multi-scaling; several key problems can be tackled at a single scale without need for bridging multiple scales. Examples include localized excitonic properties of III-V materials, and modeling response of topological insulators. However, ***real*** material phenomena are inherently multi-scale. As such, integration of modeling with experimentation and its validation requires system-specific scale-bridging efforts. Key problems of direct technological relevance that need urgent attention include i) defect microstructures and their evolution deformation, ii) plasticity and related mechanics problems, iii) nucleation and phase transformation, iii) phonon-mediated/ transport problems (solar-thermal solar cells), and iv) optoelectronic/electronic systems involving transport.

A common thread in multi-scaling efforts boils down to extension of existing as well as development of new computational algorithms. These include both scale-bridging via concurrent multi-scale approaches, and multi-physics approaches. The efforts need to be focused towards material design, as opposed to predictive modeling. In this regard, it is important that categorization of problems is need-based, not what we can get. In delineating the challenges and identifying gap areas, there must be a clear separation of spatial versus temporal multi-scaling challenges. Several problems are limited by one of the two, as opposed to both. With the continuing increase in computational resources, extending time-scale is more of an algorithmic challenge (for example, in finite difference methods such as molecular dynamics technique), and not addressed sufficiently.

The algorithmic development efforts also offer an excellent opportunity to integrate with MGI efforts through data-centric efforts. Concurrently, there is a need for development of an algorithmic genome that offers the possibility of exploring their transferability to a broader application set, and can potentially avoid method duplication. Examples that were discussed include multiphysics efforts involving interfaces, such as solidification and microstructured materials. Finally, training the next generation workforce in these efforts is a formidable challenge as exposure greatly limited, and there is an urgent need for appropriate educational materials (text books, graduate level course development) as well as educational initiatives such as NSF-NRTs.

# Closing the Feedback Loop: Integrating Synthesis, Measurement, and Computation

Moderators: Janice Musfeldt (University of Tennessee) and David Sholl (Georgia Tech)

Discussion in this break out group focused on cultural issues associated with promoting and improving feedback/collaboration between experimental and computational researchers. There is broad acceptance that this kind of collaboration is highly desirable in terms of making scientific progress and also personally satisfying for people involved in successful collaborative efforts. Our discussion focused on some ways to improve the quality of collaborative work within existing teams as well as possible avenues to encourage and promote collaboration with the objective of tightly integrating computation and experiments.

Examples were discussed of activities within collaborative teams that were specifically focused on enhancing the ability of students and postdocs to collaborate with one another. Many people highlighted the value of having regular meetings to maintain lines of communication, rather than "waiting" until there is something to discuss. The value of events that give students and postdocs autonomy was highlighted, including examples of Centers that have a student led one-day workshop before each all-hands meeting and groups that invest time specifically in non-technical team building activities.

There was considerable discussion of whether external rewards can be created that promotes the considerable effort that needs to be dedicated to make long term collaborations. While additional funding resources would of course be desirable, mechanisms that could be implemented with minimal resources were also discussed. For example, funding agencies could create recognition awards for exemplary collaboration; even modest monetary resources for awards of this kind can yield dividends.

A final issue that generated considerable discussion was the need for the community at large to encourage forthright reporting of instances where experiment and computational predictions disagree. While agreement between experiment and theory is often satisfying, disagreements between carefully performed experiments and theory often contain useful information and the seeds for future advances.

# Data: Depositories and Access

Moderators: Tim Mueller (Johns Hopkins) and Thomas Proffen (ORNL)

The attendees discussed the role of data depositories in materials research, and the associated challenges and opportunities, in five general areas:

**Sharing data**. Research groups that lack expertise in sharing databases could use assistance. It is possible to upload data to sites like The Materials Project, GitHub, and Figshare, but research groups might need guidance on how to prepare data for dissemination on these sites. Some are concerned that they might choose to upload it to the wrong site – i.e. one that does not end up being widely used. Suggested resolutions to this problem included moving to a model where there are a few large, stable data depositories that offer assistance to users who want to upload data, or to provide individual groups with standardized templates with well-defined APIs for disseminating data.

**Citing data.** There is a desire to have a standard way to cite small pieces of data. Digital Object Identifiers (DOIs) could be used, and these have an advantage in that many existing tools (e.g. Web of Science) already recognize them. For example, Oak Ridge National Laboratory is developing a system for assigning DOIs to data generated by the groups at the lab. However the data at the web site to which a DOI points could change over time and the web site could move or disappear. No good solution was found for this problem – current practice is to complain to the web site owner.

**Data curation.** Data depositories should provide high quality data or at least provide a way to assess the quality of the data. To improve data quality, a mechanism could be provided to allow users to give public feedback on the quality of data. This could be done either at the level of individual materials (e.g. to point out errors) or more broadly (e.g. to rate the overall quality of database), but it's not clear how many users would do this. It is also necessary to think about how long data should be kept – a suggested approach is to assess when the cost of storage becomes greater than the cost of reproducing the data.

**Non-crystalline materials.** The creation of data depositories for non-crystalline materials (e.g. many soft materials, amorphous materials, structural materials, etc.) lags that of crystalline materials. The challenge is that the atomic structures of these materials are not well-defined. A suggested solution is to develop a standard way to describe the processing steps used to make the material. A similar suggestion that has come up in the past is to use Materials Information Files (MIFs), which would be analogous to Crystallographic Information Files (CIFs), but more progress needs to be made.

**Data ecosystem.** It remains unclear whether the data ecosystem will (or should) evolve to consist of many small databases or a few large ones. Either way, it would be helpful to have a "Google"-type tool that facilitates finding data across databases. A suggested solution is to create a registry of materials databases. Initially this registry would be a list of existing databases, but if groups use standard APIs for disseminating their data then the registry could develop into a common user interface for searching across databases.

Based on this discussion, the following recommendations were made for next steps:

- Hold a broader workshop for data-intensive science and engineering, including researchers from data-intensive fields such as astronomy, biology, and climate science.
- Create a standard way of describing materials that aren’t easily described using atomic structure.
- Create standard APIs and templates for materials databases that can be used by individual groups.
- Create a database registry (initially just list of databases, eventually integrated through APIs).
- Identify mechanisms for maintaining data in the long term.
- Create better tools at user facilities for accessing and storing data.

## Equipping the Next Generation: Education, Training, and Outreach

Moderators: Hendrik Heinz (Akron) & Luke Shulenberger (Sandia National Laboratory)

The breakout session covered education and outreach activities across the education and career stages. Early science and engineering education was seen important in the discussion, starting at the time of Middle School. At this time, students begin to form opinions about which career to pursue. Invitations to university laboratories and opportunities for simple hands-on experiences related to Materials Science can foster interest in STEM fields. Recruitment of students from diverse ethnic and social backgrounds, in particular, minorities, for such programs was considered important. Engineering Career days for students, teachers, and parents at Universities and National Laboratories can be a great way to introduce the merits of scientific research, engage in discussions, and highlight career opportunities. Support through the MGI for summer schools as well as for science and technology projects for Middle and High School students could further aid in early education and training. Such activities can also lead to participation in pre-College science and engineering competitions such as the National Chemistry and Physics Olympiads, the Intel Science Fair, robotics competitions, and others. Engagement of teachers in summer camps, competitions, as well as in RET programs would leverage the success of such activities since continuous encouragement of students by teachers to learn more about science and engineering is expected to have higher impact than single-day activities on campus.

Education and outreach at undergraduate and graduate College level benefits from REU programs and College-level competitions (e.g. BIOMOD). It was also noted that early engagement in the freshmen year could lead to higher success rates in retaining students for science careers than in the final years. Thereby, it is not seen as a loss when students would not choose postgraduate study in their field after participating in undergraduate research; a great benefit will be increased understanding and appreciation for science as Citizens. Specifically, the success of EFRC outreach programs has been highlighted related to the integrated work environment. At the stage of postdoctoral research, delocalization of postdocs in larger groups was found particularly stimulating for research success, and sometimes encouraged by appointments as “EFRC Fellows”.

Education will increasingly benefit from the availability of online collections of pedagogical materials including websites, videos, and Massive Online Open Courses (MOOCs). MOOCs allow information from diverse areas to reach students at a wide range of places. So-called “nanodegrees” (proprietary from Udacity.com) offer certificates and modules to master certain subject areas. Similar approaches could be adopted to train computational graduate students and scientists in core compu**te**r science and data science, which are often not part of a scientific curriculum.

MGI-specific resources could also be developed, such as easy-to-access databases for materials properties, grant information, and job opportunities. The discussion also touched on the presentation of education and outreach activities as a required component of proposals to NSF. It was found that it may be more efficient to leverage existing outreach programs to provide best experiences for students rather than frequently starting new initiatives which typically require repetition and experience to mature. Outreach activities should grow naturally and be integrated into the ongoing research program as much as possible, to avoid being ‘bolted on’ to a section in a proposal.

# Community Codes and Open Source Software

Moderators: J. Lewis (WVU) and F. Gygi (UCDavis)

The breakout session on community codes and open source software gathered about a dozen participants including Steven White (UCIrvine), Aldo Romero (WVU), Paul Kent (ORNL), John Herbert (QChem) in addition to the session co-leaders.

Among the topics discussed was the question of interoperability of the software developed by the community. It was advocated that researchers should consider developing libraries rather than community codes. It was pointed out that there may sometimes be a lack of sustained interest in a particular code to get it to be developed over a sufficient time to get enough functionality.

The question of delegating technical work to programmers was debated. Several participants expressed the concern that most of the technical work requires understanding of the physics/chemistry issues involved, so that the delegation to a programmer may not be possible. This led to the question of how to educate the next generation of technicians with appropriate knowledge.

The issue of recognition of software engineering tasks in an academic environment was raised. It was suggested that code maintenance could be considered as a task equivalent to teaching in an academic institution.

Some participants expressed concern about the status of scientific computing in academic institutions, noting that scientific computing is typically not supported in computer science departments. Furthermore, it was pointed out that there is often lack of institutional support for software development in large teams.

It was also mentioned that in some instances, *sustained* support from funding agencies for a given community code may be more important than the amount of funds provided, since the skills needed to develop and maintain community software take long to acquire.

# *Abstracts*

# Collaborative Research: Chemoresponsive Liquid Crystals Based on Metal Ion-Ligand Coordination

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**Keywords:** *liquid crystals, chemoresponsiveness, anchoring transitions, chemical sensors*

### Project Scope

A new class of sensors for detection of small molecules based on chemoresponsive LCs anchored to metal surfaces has been reported, but the design of the chemoresponsive LCs has to date involved slow and laborious experiments.[1] In this project, we aim to develop a theoretical model based on thermodynamic arguments to accelerate the design of these new, highly responsive LC sensors for detection of a range of small chemical species, including HCN, $(CH_3)_2CO$, HCHO, $O_3$, CO, $NH_3$, NO, ClCN, $NO_2$, and $H_2O$. We employ novel synthesis techniques to tailor LC functionality for optimal properties in sensor applications, as predicted by first-principles computation. Experimental characterization of chemoresponsive LCs will verify their ability to detect desired target molecules and validate the computations, thus closing a cycle of prediction, synthesis and characterization.

### Relevance to MGI

This DMREF project will perform calculations in three *generations* of increasing model complexity. Synthesis and characterization will be integrated with computation in tight *cycles* built into each generation. Within a generation, calculations will identify the most promising candidate LCs for synthesis and experimental characterization. Simultaneously, new experimental observations about fundamental system properties will be integrated into more detailed theoretical models, which will advance predictions of the properties of chemoresponsive LCs to the next generation of precision.

### Technical Progress

We have successfully developed a theoretical model for the displacement of LCs from surfaces by organophosphate molecules. Using this model, we have performed a series of calculations (*Generation 1*) to predict the thermochemical binding energies of LCs and small molecules to a range of metal cation-functionalized surfaces. Several theory-predicted promising LC targets have been synthesized, and are now being characterized to determine their response to the presence of target small molecules. These measurements are providing feedback to the computational predictions.

### Future Plans

This project will continue to refine its methodology based on combining computational quantum chemistry, mesogen synthesis, and LCs property measurements to identify the most promising combinations of chemically functionalized surfaces and mesogens for design of chemoresponsive LCs. The most immediate calculations will continue to use the *Generation 1* approach, in which the effects of solvent and other environmental factors on thermochemical binding are treated implicitly by reducing the charge on metal cations by one unit relative to their formal charge in the precursor salt used in experiments. These calculations will be expanded to include the full range of analyte molecules specified in the project scope, in order to identify the most promising combinations of mesogens and metal cations for each target. Our predictions will drive synthesis of mesogens with targeted functionality, including halogen-substituted aromatics, which will be characterized and analyzed in experiments.

Our preliminary work has also shown the effect of *residual solvent* to play an important role when calculating the binding energies of LCs and analytes to metal cations. Detailed charge density analysis (see Figure 1), resulting from our quantum chemical calculations, shows that solvent effectively donates charge density to metal cations, reducing their affinity for binding LCs and analytes. The Generation 1 calculations only implicitly account for this effect by reducing the charge on metal cations by one unit. *Generation 2* calculations will explicitly include solvent molecules into the model, to more precisely account for the solvent effects and calculate more representative energetics. These calculations will also investigate solvent interactions with mesogens and analytes to determine the relevance of these interactions in calculating overall interaction energetics. In conjunction with the theoretical investigation, the role of solvent will also be investigated through controlled experiments and characterization of solvent interactions with sensor components.

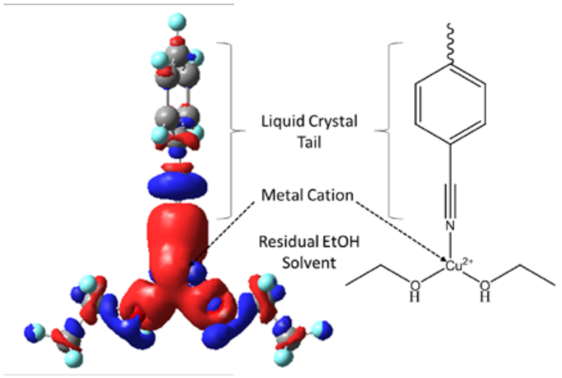

**Figure 1.** Charge density difference plot for a mesogen-metal cation interaction in the presence of ethanol solvent. Ethanol donates charge density to the metal cation, reducing its binding strength to the mesogen. Dark blue regions show charge depletion, while red regions show charge accumulation; the surface is plotted with an isovalue of 0.005 e/Å$^3$.

Preliminary experiments have also shown that the choice of anion in the precursor salt can be used to fine-tune the sensitivity of LCs to analytes. *Generation 3* calculations will explicitly treat anion interactions with the LC, analytes, and metal cations. These interactions are be small in terms of the overall energetics, but the additive effects of many anion interactions with LCs or analytes may be significant and may ultimately lead to better agreement between theory and experiment when designing future sensor systems.

### Broader impact (Optional for DOE grants/FWPs)

This project will contribute to the training of the next generation workforce by designing new materials through a multidisciplinary approach integrating computational chemistry, organic synthesis, and materials characterization. Additionally, students have the opportunity to enroll in graduate-level coursework offered by Abbott and Mavrikakis addressing the fundamental principles underlying interfacial phenomena, including the use of computational surface science methods as learning tools. The PIs will develop a new outreach activity that demonstrates the importance of integrating computation with theory at the University of Wisconsin’s Engineering Expo, which is attended annually by several thousand members of the public. This project is expected to generate intellectual property, and students will be exposed to relevant entrepreneurial activities.

### Data Management and Open Access

This project will generate a large volume of raw data (primarily from thermochemical calculations, but also including experimental characterization results) and metadata (from analyses). The data will be shared with the broader MGI community through a specially designed website modeled after the *Minnesota Database Collection* including experimental and calculated results. Our site will tabulate a wide range of data from experiment (e.g. IR spectra, binding energies from TGA, LC orientation on surfaces, NMR data for novel materials) and theory (e.g. methods, energetics, geometries, matrices of displacement for mesogens by analytes).

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# Multi-Scale Modeling and Characterization of Twinning-Induced Plasticity and Fracture in Magnesium Alloys.

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**Keywords:** Magnesium, ductility, twinning, dislocations, disclinations, crystal plasticity, anisotropy

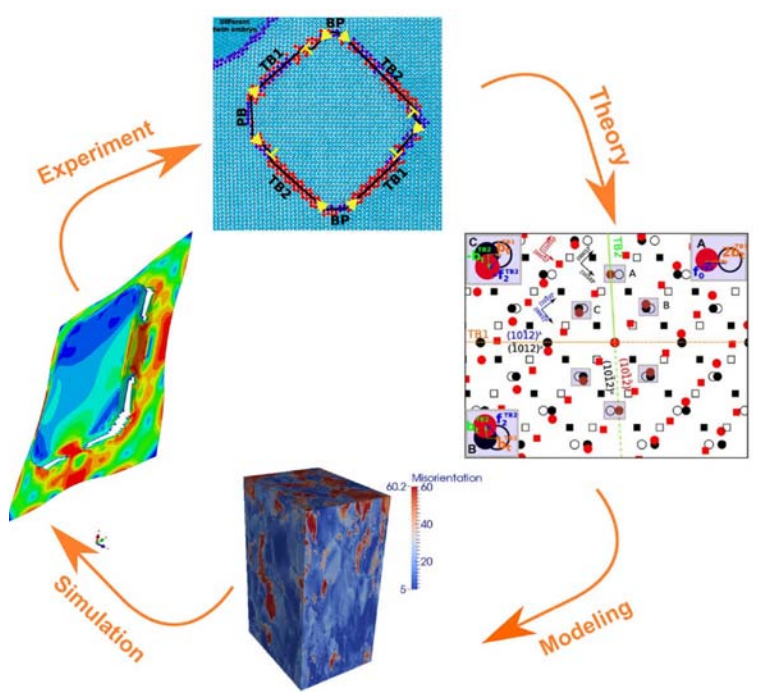

**Figure.** Theory-Modeling-Simulation-Experiment DMREF loop in Mg understanding-based design

**Project Scope** Inexpensive and rapid design of structural alloys with superior mechanical behavior is challenging because of the complex multiscale nature of the problem. This complexity is heightened in metals with non-cubic crystal structures, such as those with the hexagonal close packed (HCP) structure, which rely upon deformation twinning in order to accomplish compatible deformation in polycrystalline form. This adds to the complexity intricacies of disconnections (interfacial dislocations) and moving interfaces. Nevertheless, increasingly stringent fuel economy and emission standards force automotive manufacturers to consider lightweight HCP wrought Mg alloys in order to eke out more miles from a gallon of fuel. However, presently available alloys cannot survive conventional cold stamping operations employed in steel component manufacture, and they fracture prematurely under typical crash scenarios. This project aims to decipher the interactions between slip and twinning responsible of current impediments to the use of Mg through advanced in-situ experiments and investigations at the small (atomistic and dislocation) scale, which inspire theory required for subsequent simulations at the mesoscale. In turn, these models inform macroscale forming simulations to test the validity/applicability of the aforementioned theory in a closed loop design approach. The desired outcome is to provide a fundamental scientific basis for microstructure and alloy design which is directly tied to simulation tools necessary to implement the new materials.

**Relevance to MGI** The way and conditions under which $\{10\bar{1}2\}$ and $\{10\bar{1}1\}$ deformation twins nucleate, propagate, and interact with dislocations and each other in Mg polycrystals during plastic deformation, damage accumulation, and ultimate failure are not well understood. The manner in which alloy composition and microstructure affect deformation twinning are even more poorly understood. Deciphering the associated mechanisms will provide alloy design strategies to control plastic behavior and to mitigate damage. All these twin-related mechanisms are rooted at the atomic level. However, their dominant effect is sensed essentially at the mesoscale. MD simulations, in situ EBSD and neutron diffraction measurements, TEM imaging, and crystal plasticity simulation are being employed by the team to discover governing mechanisms and means by which to predict their impact on behavior. These ideas are beginning to displace some traditional views of twinning [c.f. 1].

**Technical Progress**

- **Atomic Scale Simulations/Theory:** Identified formal methodologies of analyzing the behavior of twin boundaries and a few important asymmetric grain boundaries, which are relevant to the dynamics of twinning. All results are generated through the molecular dynamics (MD) method. The development of a novel theory called the Trichromatic Complex, which relies on the interfacial defect approach, was necessary to decipher complex mechanisms involved in twin nucleation and mobility including: disconnection pile-up, facet nucleation, interfacial disclination nucleation, disconnection movements, disconnection transformation across interfacial disclinations, cross-faceting, and by products of interactions between lattice dislocations and twins.
- **Mesoscale Experiments:** In situ EBSD revealed mechanisms affecting damage such as twin-twin interactions, slip-twin interactions, double twinning, compression twinning, and GB-twin interactions. In situ neutron diffraction has substantiated that twins are "born" in a relaxed state. Most results are disseminated.
- **Crystal Plasticity:** Self-consistent, mean field approximations have been employed to describe the behavior of a number of current Mg alloys. A pragmatic method was first identified to incorporate deformation twinning in a full-field, three dimensional framework that uses the fast-Fourier transform modeling technique to compute the visco-plastic response of a face-centered cubic (FCC) steel with a Mn induced low stacking fault energy (SFE). Currently, these methods are being expanded to simulate HCP Mg.
- **Continuum:** Numerical methods and continuum models are being developed to simulate localization and fracture of simulated autobody parts formed under conditions close to manufacturing reality.

**Future Plans** The first two years of the program have focused on two major topical areas: 1) understanding twinning at the atomistic level using atomistic simulation and 2) developing a mesoscale understanding of twinning by employing in-situ EBSD and neutron diffraction, together with crystal plasticity modeling. During year 3 the focus has turned to 1) developing TEM evidence for or against the mechanistic concepts which have emerged from atomistic simulation, 2) transferring MD-, TEM-, and dislocation dynamics modeling-based slip-twinning interaction insights up to the mesoscale, and 3) macroscale simulation of Mg sheet forming operations.

**Broader impact** The work of numerous graduate students has been sponsored by the program. The experimental work of Jishnu Bhattacharyya (UVA) has already inspired follow-on modeling of postdoctoral researcher, Matthew Steiner (also at UVA). Fulin Wang (UVA) has begun obtaining TEM results, which are serving to validate existing modeling and inspire new modeling work (including that of collaborator, J. El Awady, at Johns Hopkins University). Christopher Barrett (MSU) has already been acknowledged as influencing the work of others (see ref. [1]). Aidin Imandoust (MSU) has been developing HRTEM skills, which target validation of atomistic simulations of Barrett et al., while Vahid Tari (MSU) has learned a great deal on fast Fourier transform crystal plasticity to capture mechanisms revealed by atomistic simulations. Akash Gupta (GTech) has already performed preliminary macroscale full-field simulations of metal forming.

**Data Management and Open Access** In addition to peer-review articles, results of various simulations and characterization are being disseminated in the ICME portal cyberinfrastructure which is Engineering Virtual Organization for CyberDesign under CAVS. The CAVS cyberinfrastructure presents a unique open access website (https://icme.hpc.msstate.edu/mediawiki/index.php/Main_Page) for reporting a free, wikipedia-type database composed of modeling and experimentations performed on various engineering materials.

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# Center for PRedictive Integrated Structural Materials Science (PRISMS)

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**Keywords:** Integrated Multi-Scale Modeling, Metals, Magnesium, Microstructural Evolution, Mechanical Behavior

### Project Scope

The primary objective of the PRISMS Center is the development and demonstration of a unique scientific platform for enabling accelerated predictive materials science. We are developing a suite of open-source integrated multi-scale computational tools for predicting the microstructural evolution and mechanical behavior of structural metals. These computational methods are being integrated with quantitative measurements from advanced experimental methods to determine model inputs, fill gaps in theory and validate simulation predictions. This new capability is being demonstrated by providing improvements to the quantitative and predictive understanding of magnesium alloys, in particular precipitate evolution and the influence of microstructure on monotonic and cyclic mechanical behavior. An important component of the PRISMS Center is the development of “The Materials Commons,” a knowledge repository and virtual collaboration space for the broader materials community.

### Relevance to MGI

The Materials Genome Initiative necessitates new collaborative and integrated modes of materials research and development. Our vision is that the platform being developed within the PRISMS Center will become an important and extensible contribution to MGI and lead to accelerated development of new materials and new materials science.

### Technical Progress

The PRISMS Center supports 11 faculty members, five staff members engaged in science and software development and 15 graduate students/post-doctoral researchers. The integrated multi-scale computational tools the Center is developing include software for statistical mechanics, real-space density functional theory, massively parallelized 3D finite element implementations of phase field, mechano-chemical transformations, crystal plasticity and continuum plasticity analysis methods, as well as software for integrating these codes and results from other advanced computational methods (e.g. dislocation dynamics) into a holistic capability. Four of these computational codes are currently being beta-tested by selected external users. The computational results are being integrated with the results of advanced experimental methods that include quantitative transmission electron microscopy and atom probe tomography, micro-digital image correlation and specialized in-situ fatigue experiments.

To ensure effective integration of PRISMS Center activities, our science objectives are organized around "use cases". These use cases provide a means to establish collaborative communities, advance science and demonstrate linkages and capabilities. The primary use cases are prediction of precipitate evolution, recrystallization and grain growth, tensile properties and cyclic/fatigue properties of Mg and Mg alloys.

Highlights of our technical progress include:

- Using the advanced PRISMS statistical mechanics software (CASM), a free energy description was developed for ordering precipitation within hcp Mg-rare earth alloys and structural transitions from ordered hcp to ordered bcc.
- Used the massively parallel PRISMS phase field code with the CASM-determined energetics to predict growth of β' precipitates in Mg-Nd alloys.
- Through high resolution imaging and quantification of chemistry and morphology of precipitates, identified key phenomena in the sequence of phase transformations taking place in Mg-Nd and Mg-Nd-X alloys.
- Completed real space DFT calculations that estimated that core-size of edge dislocation in aluminum are three times larger than indicated by conventional estimates.
- Completed the first use of PARADIS dislocation dynamics simulations to calculate strengthening from precipitates in Mg (hcp) alloy (with LLNL).
- Established methodology for modeling mechano-chemical driven phase transformations.
- Used phase field crystal model to calculate grain boundary structures and energies in 2D and compared with molecular dynamics simulations.
- Developed novel in-situ ultrasonic fatigue instrumentation to examine fatigue crack initiation and small crack growth in Mg alloys.
- Demonstrated capability of digital image correlation for quantifying heterogeneous strain distributions within grains, at grain boundaries and adjacent to twins in a precipitation hardened Mg alloy.
- Demonstrated capability of PRISMS crystal plasticity code to simulate tensile cracking at grain boundaries and fatigue crack propagation in polycrystals.

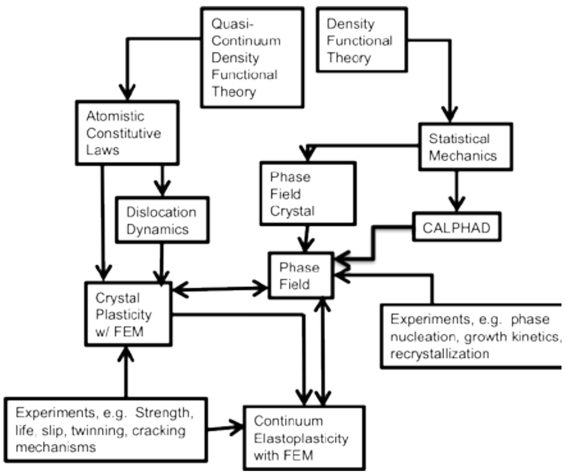

**Figure. PRISMS Framework: Integrated computational and experimental capability**

## Future Plans

The PRISMS Center will have a major open-source code release and training workshop in mid-2015 with future annual releases planned as improvements are made and new PRISMS codes developed. We have established collaborations with a number of external research groups and are actively seeking additional collaborations aligned with our use cases. Our future plans include: a comprehensive and systematic capability for integrating these advanced PRISMS codes with experiments; advanced capability for predicting phase stability and thermodynamic and kinetic properties of Mg alloys; advanced, validated capability for predicting precipitate evolution in complex Mg-Nd-X alloys; integration of results of advanced PRISMS precipitate predictions with dislocation dynamics and DFT for calculating tensile and cyclic stress-strain response of Mg alloys; modeling deformation twin formation and coupling these results with 3D crystal and continuum plasticity models and traction separation laws for predicting the influence of precipitation on grain boundary tensile fracture, local strain distributions determined by micro-DIC and local fatigue crack initiation and growth characteristics determined by the new in-situ ultrasonic fatigue capability.

## Data Management and Open Access – The Materials Commons

A key objective of the PRISMS Center is the development of the Materials Commons, an information repository and collaboration platform for the materials community. Our goal is for the Materials Commons to become a continuous, seamless part of the scientific workflow process in the technical areas being investigated within the PRISMS Center. The Materials Commons website provides an easy-to-use interface for uploading and downloading data and data provenance, searching and sharing data. At its core, the Materials Commons consists of a secure 390 TB data storage cluster, an application for efficiently uploading and downloading large data sets, and an application program interface (API) to access and extend the capabilities of the repository. The Materials Commons is currently being used internally by members of the PRISMS Center, with external beta testing commencing in early 2015 and release to the materials community planned for mid-2015.

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# Towards 3rd generation organic tandem solar cells with 20% efficiency: Accelerated discovery and rational design of carbon-based photovoltaic materials through massive distributed volunteer computing

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**Keywords:** High-throughput Virtual Screening Organic Photovoltics.

### Project Scope

The Clean Energy Project uses first principles quantum-chemical calculations to rationally design novel molecules for the next generation of organic photovoltaics, aiming to produce organic tandem solar cells with 20% power conversion efficiency. In order to perform such a large amount of quantum chemical calculations, it is necessary to have access to a large amount of computing resources, and for this we utilize idle time on distributed computers, via a screensaver mechanism. Our ultimate goal is to arrive at a systematic understanding of structure-property relations in the domain of organic electronics, for such an understanding will open the door for a truly rational design of novel carbon-based materials.

### Relevance to MGI

The Harvard Clean Energy Project is operates in a tight feedback loop with a number of experimental groups for both the design of molecular libraries and the eventual fabrication of devices. It also seeks to bridge the gap between experimental and theoretical results by developing state of the art calibration methods. These results are released publically through a web portal https://cepdb.molecularspace.org/. Recently, machine-learning techniques have been developed to rapidly screen potential molecules, greatly increasing the scope of the screening effort.

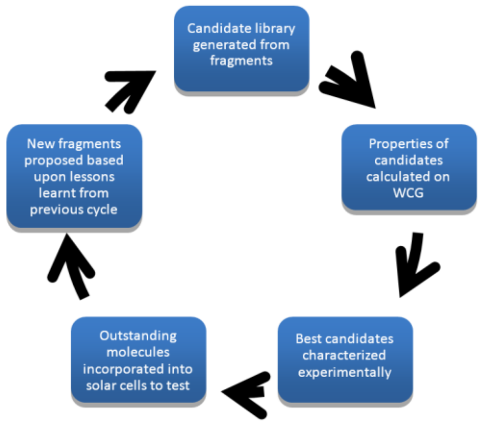

**Figure.** A positive feedback loop describing the principles used in the design of novel OPV materials

### Technical Progress

*Achievement 1: Expansion of the Harvard Clean Energy Project*. The Harvard Clean Energy Project has now screened over 3 million compounds, utilizing over 300 million quantum-chemical calculations. This represents the largest known database of such information, and the data provided affords significant insight into factors determining the efficacy of molecules for use in organic solar cells.

*Achievement 2: Complete enumeration of a library derived from experimentally suggested fragments*. A library of 2.1 million molecules has been combinatorially built from 26 fragments suggested by the Bao group (Stanford) and examined with quantum chemical calculations on the World Community Grid. The power conversion efficiencies calculated using the Scharber model have been calibrated against known experimental results, and statistically investigated. From this combinations of fragments that appear in the top performing molecules have been extracted and used to aid in the design on new libraries. The results of the analysis are shown graphically in Figure 2.

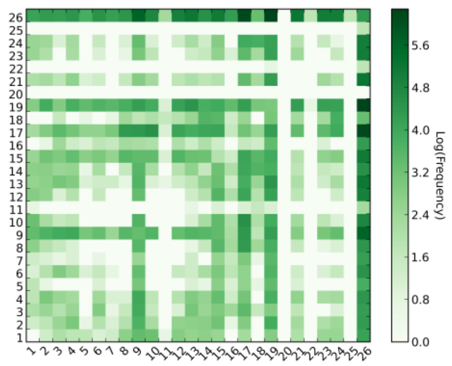

**Figure 2.** Pairwise frequencies of fragments contained within the top performing molecules can show insight into new design rules for novel organic photovoltaic materials.

*Achievement 3: Generation of libraries with greater synthetic accessibility.* One of the learning points from the initial round of investigation was of the importance of paying particular attention to synthetic accessibility of candidate molecules. This has been achieved by investigating at which sites on molecules reactions are likely to happen, and by generating libraries of molecules with specific restraints (e.g. only symmetric molecules).

*Achievement 4: Inclusion of state of the art machine learning techniques to allow for prioritization of molecules within libraries.* Collaborating with leaders from the field of machine learning, we have developed techniques based upon combining molecular fingerprinting with multi-layer perceptrons and Gaussian processes to enable the fast screening and prioritization of molecules, greatly increasing the scope of screening efforts.

*Achievement 5: Developing and benchmarking NoSQL database solutions to enable fast and flexible data storage and analysis.* In order to extract the most value from data, a sophisticated data storage solution is necessary. We have developed a NoSQL schema that is able to adapt to the changing needs of the project easily, and provides an intuitive interface which enables complex querying.

### Future Plans

*Future Plan 1: Increasing the sophistication of calibration models.* At the current time, empirical calibration is performed using a linear regression model. We plan to use multi-layer perceptrons (a type of artificial neural network) to enable the integration of molecular information into this model. The non-linear nature of this type of model should also enables increasingly tight fits between the observed data and the calibration model. We will also build models aimed at calibrating for specific types of device architecture, which should be able to capture the propensity of certain molecules to excel in certain devices.

*Future Plan 2: Using experimental pathways to guide molecule generation.* The combinatorial generation process does not always follow the same path which would be explored in the synthetic realization of candidate molecules. By using accessible starting materials and a library of robust reactions, we hope to produce libraries of molecules with suggested synthesis paths, which would aim to increase the number of candidate molecules which proceed to be realized experimentally.

*Future Plan 3: Expand the search for new molecules for organic photovoltaic devices.* Whilst complete enumeration of candidate libraries provides insight into what makes promising candidates, our recent developments in machine learning have allowed us to quickly evaluate the potential of a molecule without the need for quantum-chemical calculations. Thus we now aim to greatly expand the number of molecules investigated with only promising molecules proceeding to quantum-chemical investigation.

### Data Management and Open Access

All data is released periodically on https://cepdb.molecularspace.org/. and project scientists give regular updates on scientific and technical details on social media and the IBM World Community Grid forums.

**Publications**

Please include a list of all publications supported by this award. These papers must include an acknowledgment to the award. Manuscripts that have been submitted may be included. Do not include 'manuscripts in preparation'. We appreciate copies of these publications, which can be sent to the program managers listed below.

1. A. B. Author, C. D. Author, and E. F. Co-Author, *Title of the Publication*, Journal **Volume**, page (year).

1. Hylke B. Akkerman, Stefan Mannsfeld, Ananth Kaushik, Eric Verploegen, Luc Burnier, Arjan Zoombelt, Jonathan Saathoff, Sanghyun Hong, Sule Atahan-Evrenk, Xueliang Liu, Alán Aspuru-Guzik, Michael Toney, Paulette Clancy, and Zhenan Bao. *Journal of the American Chemical Society* **135**, 11006-11014. (2013)
2. Johannes Hachmann, Roberto Olivares-Amaya, Adrian Jinich, Anthony L. Appleton, Martin A. Blood-Forsythe, László R. Seress, Carolina Román-Salgado, Kai Trepte, Sule Atahan-Evrenk, Süleyman Er, Supriya Shrestha, Rajib Mondal, Anatoliy Sokolov, Zhenan Bao, and Alán Aspuru-Guzik. *Energy & Environmental Science* **7** 698-704. (2014)
3. Sule Atahan-Evrenk and Alán Aspuru-Guzik, Prediction and theoretical characterization of p-type organic semiconductor cyrstals for field effect transitor applications, *Topics in Current Chemistry* (2014). We also edited the volume.
4. Eric Glowacki, Halime Coskun, Martin A. Blood-Forsythe, Uwe Monkowius, Lucia Leonat, Marek Grzybowski, Daniel Gryko, Matthew S. White, Alán Aspuru-Guzik, and Niyazi S Sariciftci. *Organic Electronics* **15** 3521-3528 (2014)
5. Ying Diao, Kristina M. Lenn, Wenya Lee, Martin A. Blood-Forsythe, Jie Xu, Yisha Mao, Yeongin Kim, Julia A. Reinspach, Steve Park, Alán Aspuru-Guzik, Gi Yue, Paulette Clancy, Zhenan Bao, and Stefan C.B. Mansfield. *Journal of the American Chemical Society* (2014). Accepted.
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# Integrating Theory, Computation and Experiment to Robustly Design Complex Protein-based Nanomaterials

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**Keywords:** protein design, protein assembly, protein cages, self-assembly

## Project Scope

The overarching goal of this project is to advance new strategies for designing protein molecules that self–assemble into geometrically specific materials with sizes in the mid-nanometer range. The project elements include a theoretical foundation for how this can be achieved, computational tools for producing the amino acid sequences of novel proteins with the desired assembly properties, and experimental validation that the novel proteins assemble into the intended architectures.

## Relevance to MGI

This project encompasses all the steps from theory and design to production and experimental validation. The theory side includes an enumeration of the many possible symmetric material architectures that can be achieved by combining two simpler protein symmetries. The computational component includes the development of new software routines for designing protein interfaces under those specifications. The production component includes the expression and purification of numerous candidate amino acid sequences. The validation component includes various experimental techniques, most notably X-ray crystallography, to demonstrate the atomic level precision of the designed materials. Several successful cases have been carried from design to validation.

## Technical Progress

An underlying hypothesis of the project is that large and highly symmetric self-assembling protein materials – i.e. giant protein cages and shells – can be created by using simpler oligomeric proteins as the building blocks. Multiple strategies are possible for building higher assembly properties into such simpler building blocks. In the most general approach, amino acid sequence design is used to introduce geometrically specific protein-protein interfaces into the building blocks [1]. In another strategic variation, the higher symmetry requirements are met by combining two simpler oligomeric building blocks together by genetic fusion [2]. Both approaches have produced exciting new successes.

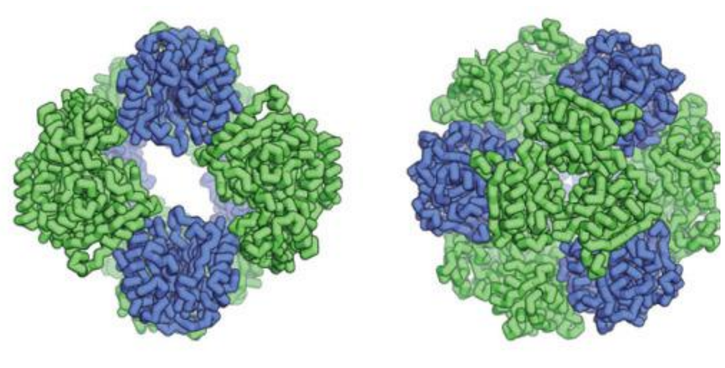

**Figure.** Crystal structure of one of the protein assemblies successfully designed in this project. Alternate views are shown down the 2-fold and 3-fold axes of the tetrahedrally symmetric structure. The diameter is approximately 130 Å. The two subunit types are shown in different colors. See ref. 2.

In work based on protein interface design, we have expanded on our initial success [1] by developing 2-component materials that assemble from multiple copies of two different protein subunit types [3]. In work published earlier this year, we focused on the design of protein cages having tetrahedral symmetry, assembling from 12 copies of each of the two subunit types, $(\alpha\beta)_{12}$; e.g. four trimers of one type occupying vertices of a tetrahedron and four trimers of the other type occupying facial positions. Such designs have diameters in the 120 to 180Å range. Using computational design methods newly incorporated into the Rosetta-Design software, 56 candidate 2-component designs were proposed. Of these, we found by negative stain electron microscopy and other biophysical experiments that five appeared to assemble essentially as intended. In order to establish more firmly whether or not the designs were successful in atomic detail, we undertook protein crystallography trials. We were able to determine crystal structures of four of the candidates. Those crystal structures showed that the observed structures were in remarkably good agreement with the designs; deviations were on average about 2Å over the protein backbones [3](see Figure).

Further success has also been established with the second design strategy based on genetic fusion of simpler oligomers. In previous work we had demonstrated the design of a 12-subunit protein assembly in the shape of a tetrahedron, 160Å in diameter [2]. In new work we demonstrated the design of a cube-shaped assembly composed of 24 identical subunits, with an outer diameter of 225Å. A crystal structure of that assembly showed agreement to the design within about 1Å deviation [4].

### Future Plans

Future efforts are being aimed at creating larger and more sophisticated assemblies, and at improving the success rate of the computational designs, which are currently in the 10% range. Concerning larger assemblies, we are part way through the process of designing one and two-component assemblies with icosahedral symmetries. Those structures have 60 copies of either one or two independent subunits. Two of these designs look promising, and one has been crystallized with diffraction observed to about 6Å resolution. These will represent new high marks for designing large protein assemblies. We are also testing the creation of extended materials – two dimensional layers and three-dimensional crystalline solids – which will obey plane group and space group symmetries.

Concerning the issue of success rate, we are exploiting the results from our design and experiment cycle to optimize the fitness functions employed in the design protocols. Preliminary indications are that some of the initially unsuccessful designs can be rescued by improving solubility, while the designed interfaces can be strengthened by improving the computational analysis of hydrogen bonding.

### Broader impact (Optional for DOE grants/FWPs)

This project is providing highly interdisciplinary training for numerous young scientists at the two supported universities. Students and postdoctoral researchers participating in the project are learning how symmetry principles apply to molecular structure, how modern computer programming can be used to design new functionalities into proteins, and how biophysical and structural methods are applied to large macromolecular complexes.

### Data Management and Open Access

The computer code in this project is being developed within the Rosetta program suite, which is publically available and licensed freely to non-commercial groups. The structural results, i.e. the atomic coordinates of the crystallographically determined structures, are being deposited in the PDB. See PDB codes 4NWO, 4NWQ, 4NWN, 4NWP, 4NWR, 4QCC.

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1. N.P. King, J.B. Bale, W. Sheffler, D.E. McNamara, S. Gonen, T. Gonen, T.O. Yeates, D. Baker D. *Accurate design of co-assembling multi-component protein nanomaterials*. Nature **510**, 103-8 (2014).
2. Y.-T. Lai, E. Reading, G.L. Hura, K.L. Tsai, A. Laganowsky, F.J. Asturias, J.A. Tainer, C.V. Robinson, T.O. Yeates. *Structure of a designed protein cage that self-assembles into a highly porous cube*. Nature Chem. **6**, 1065-71 (2014).

# Predict Blend Morphology of Organic Photovoltaic Materials

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**Keywords:** organic photovoltaics; blend morphology; Folding@home; x-ray scattering.

## Project Scope

Our work aims to address the biggest challenge that has hampered the development of organic materials for solar cell applications – prediction of the nanoscale morphology. The goal is to develop a quick, accessible framework of modeling and characterization techniques through an integrated, multidisciplinary collaboration between experimentalists and theoreticians. This will not only significantly speed-up the discovery of new high-performance organic photovoltaic (OPV) materials, but also the methodology we develop can be applied to other areas of materials research.

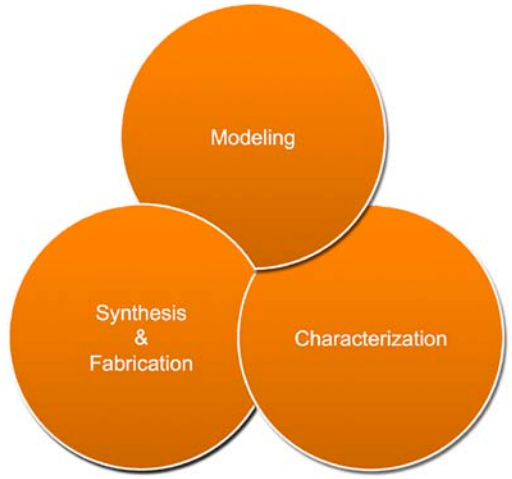

**Figure 1.** **Sc**heme showing our integrated framework for morphology prediction of organic materials.

## Relevance to MGI

Our proposed discovery pipeline will directly link the work of theory (Pande), synthesis (Bao) and morphology characterization (Toney) into a closed linked feedback loop. We will establish theoretical models and a computational framework to rapidly screen candidate compounds at a massive scale, assess their morphology, and identify structures with potential for high-performance OPVs. We will synthesize model compounds for comparison with theoretically predicted morphology and prepared promising compounds predicted by theory. We will characterize morphology of the most promising compounds and provide feedback for fine tuning the theoretical platform.

## Technical Progress

We recently initiated the project by evaluating and screening our first model materials to be utilized in both computational modeling and experimental morphology characterization. We start with a high performance blend system composed of a small molecule donor (abbreviated chemical name $(DTSPTTh_2)_2$ [1]) and acceptor ($PC_{71}BM$) in order to establish the modeling codes, because small molecules are relatively less computing power intensive than polymers and the single crystal structure and blend morphology data of this particular donor material is available in literatures for comparison. Efforts will be made to start modeling the crystal structure and morphology of $(DTSPTTh_2)_2$:$PC_{71}BM$ blends, the model thin film morphology of the blend will be characterized, and the results from the latter will be used to guide and fine tune the modeling methodology.

## Future Plans

Specific challenges will be addressed to get the simulation initialized and to make sure it converges adequately, including, but not limited to, initial simulation setup parameters, test criteria for simulation convergence, alternative strategies for simulations where convergence cannot be reached in the computational time available, handling of solvent in simulated system, and relevant timescales to reach.

Once the modeling codes are able to successfully predict blend morphology for small molecule donor materials, the blend systems will be expended to short oligomers and longer oligomers, followed by polymers with various molecular weight ranges and chemical modifications (such as side chains).

### Broader impact

Our work will establish an integrated framework for prediction of morphology of OPV materials. This research will lead to a better understanding of the materials design requirements and the gained insights will shorten the cycle for new material discoveries. Our approach is likely to also have a transformative influence on materials science and engineering in general as morphology prediction is a key challenge for many other research fields while materials properties are often strongly dependent on the morphology. The methodology developed here should be adaptable for other organic materials.

### Data Management and Open Access

Optoelectronic, structural and morphological measurements will be performed on all selected model systems. The experimental data – regardless of positive or negative outcome – will be made available to the theory group where it will be added to a collection of empirical data. The latter is utilized in calibration schemes and provides the parameterization for many of the employed models. Extending this data set will improve the related modeling efforts and their predictive capacity. This in turn will lead to a refinement in the development processes. An extensive results and reference database will serve as the hub for the information exchange between the three participating groups. The vast amount of data accumulated in the course of this project will provide the foundation for a better understanding of the molecular structure/morphology correlations, and it will be an openly available resource for the OPV community.

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# Computational Design Principles for Functional DNA-based Materials

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**Keywords:** DNA origami, structure prediction, nanoparticle synthesis, inorganic materials, plasmonics

## Project Scope

The aim of this project is to accelerate the ability to program DNA-based materials with complex nanometer scale structural features. DNA is a unique self-assembling material that offers precise control over 3D size, geometry, and curvature on sub-25nm length-scales. These objects can be used for diverse materials applications including synthesis of inorganic metallic particles with geometry and size that are prescribed in silico. Our framework is embodied in the computational software CanDo that is available for broader use online (http://cando-dna-origami.org). Success is measured by our ability to design arbitrary DNA-based nanostructures in silico that are validated experimentally.

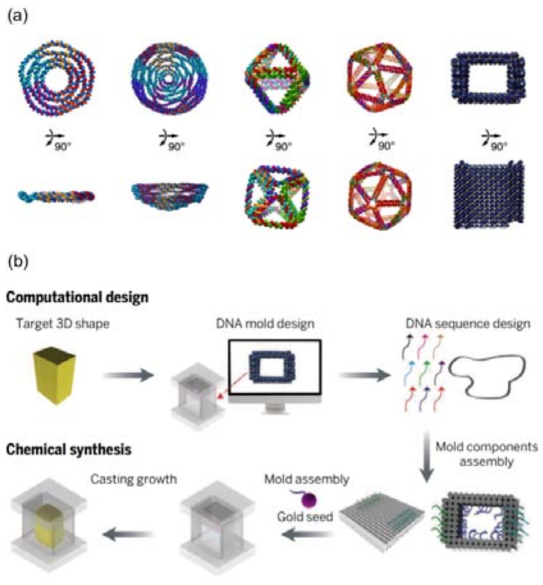

**Figure 1.** (a) Inorganic nanoparticle design and synthesis framework [2] and (b) 3D structure of complex DNA objects predicted using CanDo [1].

## Relevance to MGI

The Bathe lab is developing a computational framework for DNA-based materials design and synthesis [1] that is validated experimentally by the Yan and Yin labs. In addition to computational predictions of programmed 3D DNA structure and stability, the Bathe lab has developed computational models to predict the structure and optical properties of plasmonic nanoparticles synthesized in the Yin lab using DNA origami molds [2].

## Technical Progress

Our team recently published two articles based on this project, one in *Nature Communications* [1] that represents a major advance in our ability to program complex DNA-based nanostructures in silico (Figure 1a) and the other in *Science* [2] that represents a major advance in our ability to program inorganic nanoparticles using DNA-based molds or containers (Figure 1b). In previous work, the Bathe lab introduced the computational framework CanDo to predict the 3D structure of DNA origami objects [3]. However, that framework was overly restrictive because it was limited to origami objects designed using square or honeycomb lattice cross-sections. In contrast, many DNA objects are designed free of this lattice constraint, significantly expanding the ability to design complex architectures such as cages of arbitrary symmetries, spheroids, and discs, amongst other examples [1]. To overcome this limitation we invented a lattice-free computational design and 3D structure prediction framework that treats multi-way junctions as mechanical elements with known ground-state geometry and flexibility. Arbitrary assemblies of these multi-way junctions can then be modeled using input DNA primary sequence to predict overall 3D structure. We are in the process of implementing this framework online for broad use by the nanotechnology community. In related work, the Yin lab developed an innovative approach to cast 3D metallic particles using DNA-based containers or molds [2]. This methodology utilizes DNA origami molds that are designed in silico to ensure maximal structural integrity that limits the particle growth during synthesis. In particular, we found that origami molds made only of a single layer of double-helices do not have sufficient mechanical stiffness to resist the outward pressure due to the growing particle, and therefore do not maintain shape fidelity successfully. In contrast, multi-layer container walls consisting of at least two helices were found to be sufficiently rigid. Thus, computational 3D structure prediction together with mechanical property analysis enabled proper mold design [2]. Further, the Bathe lab used optical property simulations of the metallic nanoparticles to demonstrate that experimental Electron Energy Loss Spectroscopy measurements were consistent with model predictions. Finally, they used electromagnetism simulations to compute the plasmonic properties of the particles in solution [2], demonstrating their potential for biomolecular sensing and other applications related to plasmon resonance.

## Future Plans

The principal aim of this work is to expand and refine our ability to predict 3D structure and stability of programmed nanoscale DNA assemblies. An important step in this direction was achieved with our recent publication [1] that demonstrates significantly broader scope of 3D structure prediction than was previously possible [3]. This publication also integrates sequence-based design of DNA nanostructures, which was not part of the previous CanDo framework. Future work will seek to expand CanDo to include arbitrary DNA-based assemblies including multi-way junctions and single-stranded crossovers. In addition, sequence design for optimal folding and yield of arbitrary DNA nanostructures under diverse buffer conditions is also being pursued.

## Broader impact

Dissemination of our computational framework CanDo to the broader scientific community via the online server cando-dna-origmi.org enables broadest use of DNA-based assembly to design de novo nanoscale materials for diverse target applications in materials science and technology. Training undergraduate and graduate students in integrated experimental-computational approaches to materials structure and property prediction in the PI's laboratories aids in educating the next generation workforce in nanoscale materials science and nanotechnology.

## Data Management and Open Access

Our computational developments in 3D structure prediction of DNA origami objects are available online at the CanDo server: http://cando-dna-origami.org. We are additionally posting computational scripts there related to material property calculations such as plasmonic properties, Electron Energy Loss Spectroscopy, and others.

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# Multi-Scale Fundamental Investigation of Sintering Anisotropy

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**Keywords:** Sintering, Anisotropy, Multi-Scale Modeling; Pore Morphology.

### Project Scope

This research program will develop a new generalized multi-scale theory of sintering of particulate materials that takes into account anisotropy phenomena. It will provide impetus to the development of full-fledged multi-scale virtual reality (supported and verified by experiments) of the material during sintering - a critical manufacturing step in advanced ceramics and some metals. The anticipated outcome of the research is an integrated modeling and experimental framework taking into account the complex interplay between processing conditions and anisotropic microstructure development. This basic understanding will provide novel practical approaches to optimize the sintering with programmable macroscopic characteristics and microstructure.

### Relevance to MGI

In this project, the constitutive relationships for sintered materials are obtained through numerical experiments in the virtual test environment and validated experimentally. In an iterative manner, the constitutive relationships are used to predict and experimentally validate the evolution of anisotropic microstructure during sintering. Our research will lead to a rational approach to optimize the manufacturing of complex sintering systems leading to accelerated development and insertion of new materials and processes in critically important technologies – a goal of MGI.

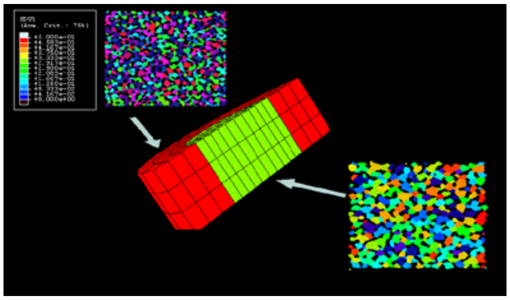

**Figure 1.** Multi-scale modeling of sintering.

### Technical Progress

Theoretical analyses of shrinkage and distortion kinetics during sintering of bilayered porous structures has been carried out. The developed modeling framework is based on the continuum theory of sintering; it enables the direct assessment of the cofiring process outcomes and of the impact of process controlling parameters. The derived “master sintering curve”-type solutions are capable of describing and optimizing the generic sintering shrinkage and distortion kinetics for various material systems. The approach utilizes the material-specific parameters, which define the relative kinetics of layer shrinkages such as the relative intensity of sintering, and employs the conversion between real and specific times of sintering. The obtained theoretical results have been compared to the experimental data based on the optical dilatometry of mono- and bi-layered porous structures.

A novel methodology has been developed for the determination of the ratio of the shear viscosities of the layer’s fully dense materials. Experimental analyses of shrinkage and distortion kinetics during sintering of bilayered porous and dense gadolinium-doped ceria Ce0.9Gd0.1O1.95d structures have been carried out, and compared with the developed theoretical models. The experimental results of shape distortion and shrinkage kinetics are in excellent agreement with the modeling predictions. A model, which describes the combined effect of sintering and gravity of thin multilayers, has been derived and compared with experimental results. It allows for consideration of both uniaxial and biaxial stress states. The model is based on the viscous sintering framework, the classical laminate theory and the elastic-viscoelastic correspondence principle. The modeling approach is then applied to illustrate the effect of gravity during sintering of thin layers of cerium gadolinium oxide (CGO), and it is found to be significant.

Carefully controlled experiments have shown that under non-hydrostatic stresses (as are developed during constrained sintering of multilayers and which are externally imposed in many sintering practices like sinter-forging), an initially isotropic microstructure becomes anisotropic. In a new finding we have shown that under a compressive uniaxial stress, intrinsic pores (pores of the order of the particle size) orient parallel to the applied stress and extrinsic pores (pores at least an order of magnitude larger than particle size orient perpendicular to the applied stress.

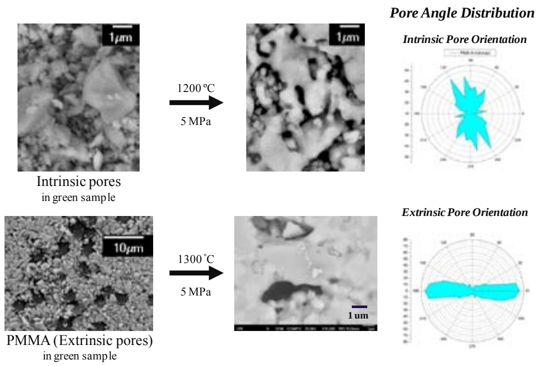

**Figure 2.** Evolution of Intrinsic and Extrinsic Pores in Cathodes during Stress-Assisted Sintering (stress direction vertical in these pictures)

## Future Plans

We plan to continue the analysis of the multi-layered systems' sintering at the macroscopic level and to combine the mesoscopic level analysis of the in-sintering pore-grain structure evolution with macroscopic continuum modeling of sintering of real-world powder components. We will also continue to focus on the anisotropic microstructural evolution during stress-assisted sintering. The technological application of our research activities will be related to high performance electrochemical systems (e.g. electrodes for solid oxide fuel cells, gas separation membranes and batteries) which have microstructural requirements that include high surface area and porosity. These requirements are seemingly contradictory to the conditions for reliable and stable long-term performance. This apparent contradiction can be addressed by using graded, hierarchical and/or anisotropic porous microstructures.

## Broader impact

The conducted research is focused on the development of a new approach to optimize the sintering of a broad range of complex material systems including for example multilayered solid oxide fuel cells. This methodology can be used to design the processing of other multilayered material systems (e.g. sensors, actuators, solar cell packaging) or processing under applied stresses (e.g. hot-pressing, sinter-forging). The integrated, collaborative research program provides a unique high quality learning opportunity for our students. At San Diego State University, this research program contributes to the development of the two Joint Doctoral Programs: in Engineering Sciences and in Computational Sciences. The research team involves students from underrepresented groups in this research program. The industrial partners participate in the model-verifying experimentation on the sintering of multi-layered solid oxide fuel cell components. Saint-Gobain provides also continuous guidance and advise on the selection of materials and process parameters. As a result of this integrated approach, all the students and post docs working on this project are exposed to the iterative simulation-experimental approach of conducting research – a critical element of the MGI.

## Data Management and Open Access

The research results are submitted to NSF as reports, posted on the PI lab's web sites, published in scientific periodicals and presented at technical meetings. Published data under this award such as articles, dissertations, are accessible from publishers or upon request to the senior and student researchers involved. The primary analyzed data produced under this award as well as the associated metadata that describes the theoretical models and data analysis methods, experimental setups, fabrication procedures, are made publicly available. Data on the densification and deformation characteristics of the investigated materials over a range of temperatures, anisotropy factors and green density are being generated. The raw results are analyzed using standard practices and submitted in technical reports and publications for open dissemination.

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# Control of colloidal assemblies using dynamic DNA nanostructures

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Keywords: DNA, self-assembly, nanotechnology, origami, responsive materials

## Project Scope

This project seeks to develop a fundamental understanding of how (dynamic) DNA nanostructures can control and program colloidal self-assembly, and, by putting this concept on a strong fundamental footing, to exploit it to maximum effect, through the design of DNA reaction networks that solve essential challenges to making colloidal self-assembly a practical materials fabrication platform. We aim to both discover the fundamental principles underlying DNA particle-nanostructure interactions, and create new materials, from plasmonic molecules to metafluids. Success will be measured by how well the structure and response of the experimentally produced assemblies can be predicted by theoretically-derived design rules.

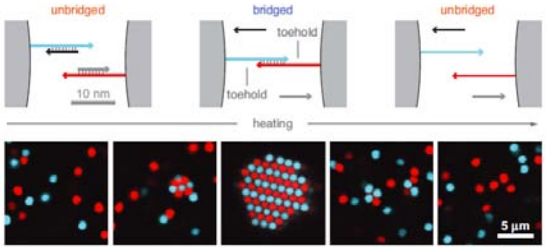

Figure. DNA strand displacement can be used to program a re-entrant melting transition in a suspension of DNA-grafted colloidal particles. The confocal micrographs at bottom show a colloidal crystal that nucleates and grows from the fluid upon heating [1].

## Relevance to MGI

This project involves close work between an expert in colloidal particle physics (Manoharan), an expert in DNA nanostructure fabrication (Shih) and an applied mathematician with expertise in theoretical and computational models of self-assembly (Brenner). Theoretical models from the Brenner group will be used to first predict qualitative features (such as geometry) of DNA nanostructures that are suitable for combining with colloidal particles. Shih's lab will then synthesize such nanostructures. Manoharan's lab will then prepare DNA-colloid hybrid systems and measure properties such as assembly dynamics and melting characteristics. Brenner's computational models will be updated with the results of such experiments and predict parameter regimes for the next round of experiments.

## Technical Progress

In recent work [1] we have succeeded in using DNA strand displacement, a reaction between free DNA strands in solution and DNA strands grafted to colloidal particles, to create colloids with programmable phase transitions. By changing the number and concentration of displacing strands, we have designed colloidal suspensions that can melt upon cooling or reversibly switch between two different crystal structures. This method represents a new direction in DNA-mediated colloidal assembly, in which information supplied to the buffer (in the form of the displacing strands) programs equilibrium pathways between many different target structures. Recent theoretical work has exposed a new method, the principle of undesired usage, for designing structures built with specific interactions to have high yield [2].

## Future Plans

The free energy provided by DNA strand displacement reactions can be used to power novel structural transformations common in natural systems but not typically seen in synthetic constructs. We plan to investigate two such possibilities – self-replication and autonomous error correction in structures. Self-replication in colloidal assemblies can allow for selection-amplification cycles that lead to discovery of novel functionalities that cannot be realized easily otherwise. We plan to realize such self-replicating cycles using DNA dynamic nanostructures and colloidal assembly, guided by published simulation work from the Brenner group. The central ingredients needed are time-dependent specific interactions between colloidal particles; such interactions allow a parent structure to induce the assembly of a new child structure that can then separate from it. We will create such interactions between colloidal particles using DNA nanostructures that undergo strand displacement reactions.

We are also studying the use of free energy stored in DNA nanostructures to correct errors in assembly, mimicking analogous proofreading processes seen in biology such in the ribosome during protein synthesis. We are presently focused on `proofreading' errors in the hybridization of almost complementary DNA strands, a central problem of biomedical significance. We are studying the sequence design problem for DNA strand displacement reactions that can disrupt and undo erroneous hybridization.

A challenge for for colloidal assembly is to generate microparticles with spatial addressability rivaling that seen for DNA nanostructures. To meet this challenge, we are assembling DNA-origami harnesses that are designed to wrap around microparticles. Thus the microparticle serves to "inflate" the DNA harness to improve structural integrity, while the DNA nanoharness provides uniquely positioned sequence features that provide spatial addressability.

## Broader impact (Optional for DOE grants/FWPs)

The broader impacts of the project include the training of graduate students and postdocs from experimental physics, biology, physics and mathematics in an interdisciplinary environment, as well as a program developing a design curriculum for inner city middle schools in Cambridge, MA. Undergraduate teams will develop computational tools for the project through a summer program run through Harvard's Institute for Applied Computational Science.

## Data Management and Open Access

All computational frameworks developed in this project will be made widely available, with source code, on github.com, a site that allows multiple users to contribute code, report bugs, and suggest enhancements to open-source software projects. DNA sequences and protocols used in the experiments will be made publically available through the world-wide web.

## References

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# Molecular Electrocatalysis for Hydrogen Production: Make, Measure and Model at its Best

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**Keywords:** Molecular Electrocatalysis, Hydrogen Production, Nickel Phosphine Complexes, Proton Relays, Coordination Spheres

## Project Scope

*The Center for Molecular Electrocatalysis' (CME) overarching objective is to develop a fundamental understanding of proton transfer reactions that will lead to transformational changes in our ability to design molecular electrocatalysts for interconversion of electricity and fuels*. We seek to understand, predict, and control the intramolecular and intermolecular flow of protons in electrocatalytic multi-proton, multi-electron processes of critical importance in energy transformation reactions required for a secure energy future: the production of $H_2$, the oxidation of $H_2$, the reduction of $O_2$, and the reduction of $N_2$. Our research focuses on earth-abundant metal catalysts as cost-effective alternatives to precious metals.

## Relevance to MGI

The CME The strong collaboration between experiment and theory in the CME has lead to the development of a comprehensive thermodynamic and kinetic model with predictive capabilities based on three simply determined experimental variables. This allows for rapid screening of synthetic targets for optimum catalytic performance given a desired set of conditions.

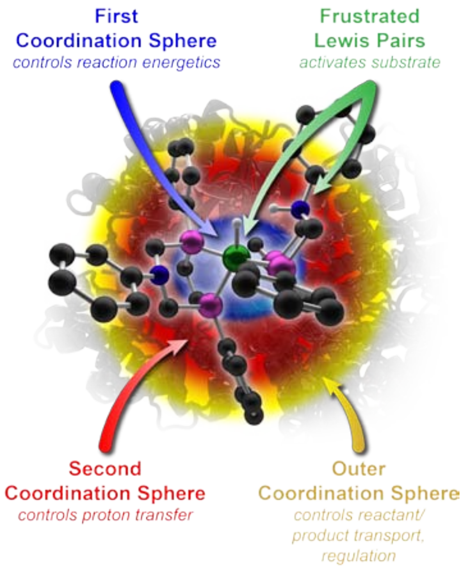

**Figure 1.** Careful design of the coordination spheres to control proton movement to and from molecular electrocatalysts for $H_2$ production leads to efficient and rapid catalysis.

## Technical Progress

The CME has developed molecular Ni-complexes for electrocatalytic $H_2$ production with TOFs as high as $6\times10^7\ s^{-1}$, catalysts for $H_2$ oxidation with rates as high as $60\ s^{-1}$, and catalysts capable of reversibly oxidizing and producing $H_2$ with overpotentials <100 mV. These achievements are the result of an increased understanding of the principles for controlling proton movement, from H-H bond cleavage and formation to intermolecular proton transfer. The CME uses a team approach to understand all the aspects of molecular electrocatalytic $H_2$ production and oxidation, including synthesis of new ligands and catalysts, electrochemical and electrocatalytic studies, quantification of multiple dynamic processes by NMR spectroscopy, thermochemical studies, and a detailed understanding of each step using advanced theoretical methods. The culmination of these CME studies on Ni-based electrocatalysts provides arguably the most detailed understanding of *any* electrocatalytic system.

The hydride donor ability of Ni hydride complexes and acidity of proton relays can be used to control the free energy for the addition of $H_2$ to $Ni^{2+}$ complexes, $\Delta G^\circ_{H2}$. This parameter determines if the catalyst will function as an $H_2$ production catalyst ($\Delta G^\circ_{H2} > 0$), an $H_2$ oxidation catalyst ($\Delta G^\circ_{H2} < 0$), or a reversible catalyst ($\Delta G^\circ_{H2} \approx 0$).

Optimal catalytic rates are achieved when the p*K*a of the exogenous acid used for catalysis matches the p*K*a of the protonated intermediates in the catalytic cycle.

We have successfully established the capability to calculate thermochemical values *a priori* with an accuracy rarely reported in the literature (p*K*a values accurate to ~1 p*K*a unit, hydride donor abilities accurate to ~1.5 kcal/mol, and redox potentials $E°$ accurate to ~0.06 V). This capability has been employed to calculate the complete set of thermodynamic properties that govern the chemistry of the molecular Ni-catalysts for $H_2$ oxidation and production. The data and correlations among them can be used to predict the relative free energies of all catalytic intermediates based on three easily determined quantities (two $E°$ values and one p*K*a value). The derived "free energy maps" and approach are general and powerful, allowing prediction and optimization of catalyst performance.

**Future Plans**

In addition to altering catalyst structure increasing catalyst performance, we also plan on changing the catalyst medium to facilitate proton movement. We have observed increases in catalytic rates for $H_2$ production by factors as high as 105 upon addition of water to acetonitrile or protic ionic liquids *without* a corresponding increase in overpotentials. Preliminary results show that specific combinations of catalyst structure and protic ionic liquid exhibit uniquely high activity with TOFs exceeding $6 \times 10^7$ $s^{-1}$, an increase of five orders of magnitude relative to the same catalyst in acidic acetonitrile solutions.

The CME will also extended the concept of using proton relays to design molecular catalysts into developing active electrocatalysts for $H_2$ production based on Co, Fe and Mn complexes and for $H_2$ oxidation.

**Selected Publications**

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# First-Principles Based Design of Spintronic Materials and Devices

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**Keywords:** Heusler, Half-Metal, Slater-Pauling, Spintronics, Formation energy

## Project Scope

We have studied three families of Heusler alloys. These materials were chosen because of their tendency to generate half-metals. A half-metal is a conductor for one spin-channel, but an insulator for the other. The gap in the density of states tends to occur with precisely 3 occupied bands per atom in the gapped channel. We have calculated the electronic and magnetic structure, and the formation energy for nearly 1000 alloys. We have selected a subset of these alloys for experimental investigation through synthesis, and characterization. Several important principles useful for guiding the search for spintronic materials emerge from our studies.

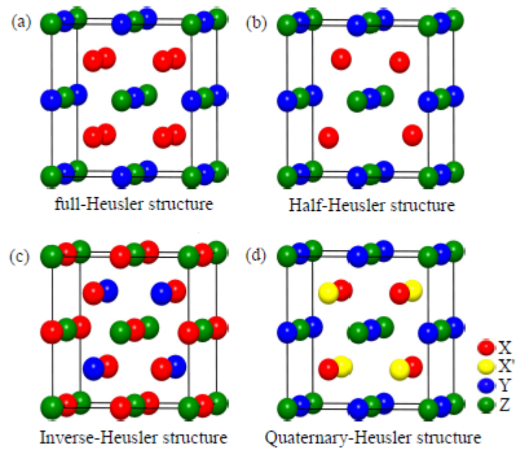

**Figure.** Three families of Heusler alloys (a-c) and a quaternary Heusler alloy (d)

## Relevance to MGI

Our project utilizes a close, iterative feedback loop between synthesis/processing, properties/measurement, and theory/modeling. Our database of calculated properties is examined for interesting new alloys that have calculated formation and ordering energies that indicate they may be synthesized. The alloys are synthesized by arc melting and annealing and by sputter deposition and annealing. After synthesis they are characterized by X-ray diffraction, metallography, scanning electron microscopy, electron dispersive spectroscopy, and magnetometry. Often, as we illustrate below, additional first-principles calculations are used to better understand the results of synthesis processing and characterization.

## Technical Progress

We used first-principles electronic structure techniques to calculate the electronic and magnetic structure, and formation energy of 270 full Heusler alloys, 378 half-Heusler alloys and 405 inverse Heusler alloys. The energy difference between the full Heusler alloys and the inverse Heusler alloys provided an estimate of their odering energies. These alloys are intriguing because of a tendency to place a band gap near the center of the d-bands. For full and half-Heuslers and many inverse Heuslers, this gap (or near gap) occurs for 3 occupied states per atom in the gapped channel. Our study provides evidence that if the Fermi energy falls in or near the gap this reduces the energy of the system and seems to be the primary reason these rather strange (especially the half-Heusler) structures are energetically favorable. Indeed, we find that the most stable (lowest formation energy) Heusler structures tend to be those with 24 electrons for full Heuslers or 18 electrons for half-Heuslers because these alloys can generate a gap in both spin-channels, i.e. they can form Slater-Pauling semiconductors.

A second important discovery has been the prediction that different half-metallic Heusler alloys can be layered and still retain their half-metallic property. Computationally, if we layer different half-metallic Heusler alloys along (001), (110) or (111) directions the layered system is usually also half-metallic. This implies that an infinite number of half-metallic structures are, in principle, available for spintronic applications. Furthermore, the layering introduces uniaxial anisotropy and makes it possible to generate perpendicular magnetocrystalline anisotropy, a property that is needed for many spintronic applications. It also makes it possible to combine Slater-Pauling half-metals with Slater-Pauling semiconductors to make all-Heusler magnetic tunnel junctions.

Our recent experimental results indicate that this layering sometimes occurs naturally. Our experimental team synthesized $Fe_2TiSb$ because we predicted it to be half-metallic and no reports of previous investigations were found. The expected $L2_1$ structure was confirmed by XRD. However, the stoichiometry seemed to be $Fe_{1.5}TiSb$, instead of $Fe_2TiSb$. Additional calculations indicated that the half-Heusler FeTiSb was also stable. Our current analysis of this structure indicates that it can be viewed as $Fe_2TiSb$ with an ordered sublattice of Fe vacancies. This is equivalent to a layered system with alternate layers of FeTiSb and Fe2TiSb. This layered system appears to form on annealing of bulk systems. We calculate that the formation of this layered system (or ordered vacancy sublattice) lowers the system energy. It also generates a Slater-Pauling semiconductor which we believe to be the driving force behind the reduced energy.

## Future Plans

We want to better understand the origin of the band gaps and half-metallicity that are common in Heusler alloys. We also want to investigate the multiple solutions to the DFT equations that are common in these systems. We would like to fabricate a zero moment half-metal. We plan to investigate layered Heusler heterostructures for giant magnetoresistive (GMR) and tunneling magnetoresistive (TMR) devices as well as for spin-injection into semiconductors.

## Broader impact (Optional for DOE grants/FWPs)

Half-metallic Heusler alloys and heterostructures offer the potential for important advances in digital memory applications and (more speculatively) for spintronic digital logic.

## Data Management and Open Access

NIST has indicated an interest in hosting our databases as part of their participation in the MGI. We are also investigating other alternatives.

## Publications

1. K. Munira, J. Romero, and W. H. Butler *Achieving perpendicular anisotropy in half-metallic Heusler alloys for spin device applications*, Journal of Applied Physics **115,** 17B731 (2014)
2. A. Singh, S. Schwarm, O. Mryasov, and S. Gupta, *Interlayer exchange coupled composite free layer for CoFeB/MgO based perpendicular magnetic tunnel junctions*, Journal of Applied Physics, **114**, 203901 (2013).
3. A. Singh, S. Gupta, M. Kuteifan, M. Lubarda, V. Lomakin and O. Mryasov, *Effect of interlayer exchange coupling parameter on switching time and critical current density in composite free layer*, Journal of Applied Physics, **115**, 17D111 (2013).

# Materials Engineering of Chromonic and Colloidal Liquid Crystals via Mathematical Modeling and Simulation

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**Keywords:** Liquid crystals, defects, colloids, chromonic phases, electrophoresis.

### Project Scope

The goal of this project is the study of liquid crystal colloids and chromonic phases. The interaction between colloidal particles and the liquid crystal matrix brings out significantly different phenomena than that encountered in isotropic colloids. It turns out that the interaction between liquid crystal anchoring on particle surfaces and on confinement walls brings out topological defects in the matrix that generate new forces able to compete, for instance, with gravitational and electromagnetic ones. Accounting for the presence of ionic particles in the liquid crystal is also a goal of the research. For this, new models of liquid crystals with embedded particles and ionic effects need to be developed, analyzed numerically simulated. The PI's aim at arriving at a quantitative description of nonlinear, AC driven, electrophoresis, as well as understanding mechanisms of packing and clustering in biology.

### Relevance to MGI

The Pis assemble a team of researchers that can synergistically address the major topics of investigation. It includes experimental expertise on the preparation and analysis of such suspensions, in particular, for the novel case of a chromonic, and the analysis of the response of the suspension to external fields. Experts in mathematics and physical modeling of complex fluids will develop the necessary extensions of existing phenomenology to consider charged systems, ensembles of particles, and deformable surfaces (as appropriate for chromonics), as well as related phase field formulations. A great deal of static and dynamic information can be extracted not from a field based description, but rather from a particle type description that is based on topological defect motion. The group also has extensive computational expertise in the development and implementation of numerical schemes to study static and dynamic phenomena in complex fluids.

### Technical Progress

The PIs have made progress in the following topics: (1) Development of a finite element methods to study defects found in colloidal matrices, in particular, saturn rings and hedgehog point defects, (2) Static simulations of defects, (3) Development of a dynamic model for ionic liquid crystals. Recently, PI Lavrentovich has published a survey on *Liquid crystal enabled electrophoresis and electro-osmosis* [1], that presents electrokinetic phenomena of liquid crystals, with the state-of-the-art description of experiments, some developed since the submission of the proposal. This will serve as a route map for modeling and the iterative procedure modeling-simulation-experiment. As a new insight, we will be able to separate electrophoresis from electro-osmosis.

**Future Plans**

1. In the area of liquid crystal electrokinetics, one main emphasis is to obtain analytic and numerical predictions of the quadratic dependence of the flow velocities on the applied electric field. This provides the opportunity to obtain steady motion of an electrically charged fluid with alternating electric current.

2. We also address the motion of a single colloidal particle in the charged liquid crystal, in order to understand the basis of liquid crystal-enabled electrophoresis. One main difference with the isotropic analog is the role of the anchoring of the liquid crystal on the surface of the particle and the subsequent bulk defects and the associated forcing fields that this may cause.

3. Another line of research is the study of liquid crystal-enabled electro-osmosis, that is, the motion of the liquid crystal itself around a fixed particle. In particular, we will address the problem of liquid crystal flow passed an obstacle, that is, the analog of the Stokes problem of an isotropic fluid.

From the mathematical point of view, the equations governing liquid crystal electrokinetics share the structure of the PNP equations for isotropic fluids, with the Leslie-Ericksen system of nematic liquid crystals. However, the nonlinear effects of the liquid crystal case are strongly enhanced by the charge separation induced by liquid crystal alignment.

4. Develop finite element methods to model topological defects according to the Landau-de Gennes model, in the case that the gradient operator involves terms that may become degenerate in the isotropic phase.

5. Development of order parameter models for the motion of line defects in the liquid crystal.

6. Study static packing shapes of chromonic liquid crystals in connection with recent experiments carried out by the group of PI Lavrentovich.

All Pis are involved in the different research topics, but with a main individual concentration on special ones. The problems are discussed in WebEx group meetings that take place every other week. In addition to the Pis, graduate students and young researchers are also involved.

**Broader impact**

Currently, the project involves three graduate students (advisers: Calderer, Lavrentovich and Vinals) and an associated researcher (Lavrentovich):

1. Paula Dassbach (Calderer, Mathematics) works on the experimentally observed *levitation problem:* a colloidal particle on a liquid crystal matrix may float instead of sinking to the bottom of the container. This is due to the force exerted by topological defects in the liquid crystal. She is developing a finite element method to model the system and calculate the force due to defects. Paula Dassbach passed the *Preliminary oral examination* last November.
2. Chris Conkling (Vinals, Physics) works on simulations of defects. He has recently got involved with the electrokinetics project as well. Chris Conklin passed the *Preliminary oral examination* in December.

**Data Management and Open Access**

An MGI conference is being planned for next fall. Details are still premature.

**Publications**

1. Oleg D. Lavrentovich, *Liquid crystals-enabled electrophoresis and electro-osmosis*, Preprint, (2015).

# High-Throughput Discovery, Development and Demonstration of Material Systems to Enable Low-Power NEMS-Based Computation

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**M.P. de Boer**, Department of Mechanical Engineering, Carnegie Mellon University
**G. Piazza**, Department of Electrical and Computer Engineering, Carnegie Mellon University

**Keywords:** Nanoelectromechanical systems, tribology, TP, electrical contacts, surface contamination.

## Project Scope

Transistors are very energy-inefficient. Radically different designs are needed to replace or complement transistors to enable low power computing. One is the nanoelectromechanical (NEMS) switch (Fig. 1), which *physically* opens and closes to turn signals on and off. These can be $10^6$ times more energy efficient, but suffer from reliability problems as the contacting electrodes must cycle up to $10^{15}$ times without wear or contamination. Materials and environments which do this do not yet exist. Our objectives are: (1) to understand NEMS switch failure mechanisms; and (2) to develop materials and operating conditions with ultra-high reliability.

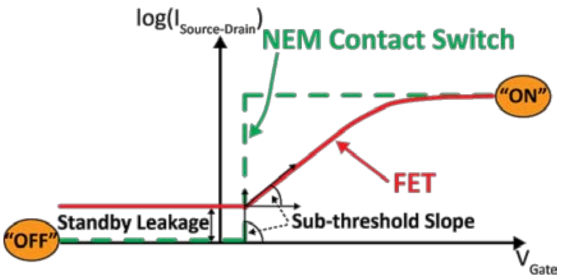

**Fig. 1.** Solid-state field-effect transistors (FETs) are fundamentally limited by a low substhreshold slope and high standby leakeage. NEMS switches overcome both of these limitations to save energy.

## Relevance to MGI

We integrate computational modeling of atomic-scale failure mechanisms with nanoscale experiments for high-throughput screening of NEMS electrode materials and operating conditions. We are characterizing existing Pt-based electrodes to identify a set of descriptors to apply to new candidates materials. From these candidates we are selecting ones with required characteristics including electrical conductivity, wear resistance, and resistance to oxidation and buildup of tribopolymer (TP) contamination. The most promising candidates will be tested in prototype nanoscale devices to ultimately identify materials and conditions that enable NEMS technology.

## Technical Progress

The project involves five integrated thrusts: 1. Contact material development/characterization; 2. Quantum chemical simulations of TP formation; 3. Molecular dynamics simulations of TP formation; 4. Study of contamination resistance in ohmic microswitch contacts; and 5. Development of NEMS switches. **Contact material development** focused on characterizing $Pt_xSi$ ($1 \leq x \leq 3$) as a candidate material. This was identified as a candidate based on an early, basic screening process based on its high electrical conductivity, higher modulus and hardness than Pt, and a hypothesis (supported by DFT) that it would be less susceptible to contamination. Both source-controlled and kinetically-limited solid-state diffusion were used to precisely tune the silicide phase. We obtained high phase purity (up to 90%) and demonstrated higher modulus and hardness than Pt. **Quantum chemical simulations** investigated how TP formation on multiple NEMS electrode surfaces using DFT. Overall, we aim to determine how TPs form, and from this, recommend contamination-immune materials. We demonstrated a pressure effect on TP (polymerized benzene) formation. The threshold polymerization pressure reduces on reactive metal surfaces due to catalytic behavior. Importantly, this provides the new guidance for the rational development of electrode materials for NEMS switch contacts based on surface chemical activity. **Molecular dynamics simulations** focused on developing a new MD method for single asperity contacts in metals. The key objective is to determine the effects of hydrocarbons on mechanical asperity contact and to investigate the effects of hydrocarbon characteristics (molecule size, adhesion, viscosity, film thickness, *etc.*). Preliminary results were obtained for the evolution of the contacts with and without the introduction of a thin film of hydrocarbon molecules as well as for the influence of hydrocarbon films on the force-displacement curves.

**Contamination resistance in microswitches** focused on (i) determining contaminant concentration thresholds of Pt and $RuO_2$ (another candidate material) contacts that initiate electrical degradation while testing in backgrounds with maximal TP immunity ($N_2$ for Pt, $N_2$:$O_2$ for $RuO_2$) (ii) investigating electrical, chemical, and structural characteristics of tribopolymer and while improving conductivity and (iii) investigating temperature and current effects on the deposit. The contamination threshold for TP formation is much higher for $RuO_2$ in an $N_2$:$O_2$ background than Pt in a $N_2$ background. If a Pt-coated switch has degraded electrically in $N_2$-$C_6H_6$ , its contact resistance can be restored nearly to its original level by re-introducing $O_2$. Raman suggests that $O_2$ increases the TP's graphitic content. Under some conditions, a passivating conductive layer is created that protects the surface and extend device life by $10^3$ times. Also, in some environments, increasing temperature inhibits growth, and passage of electrical current augments the quantity produced while also making it conductive. **NEMS relay development** involved design/evaluation of two topologies for contact material insertion. Cantilever and buckling beam designs were compared according to scalability, actuation voltage, and fabrication ease. Both topologies were demonstrated, including relays made with 10 nm AlN piezoelectric films. A third topology was conceived and is under development.

## Future Plans

Next, we will complete theory and experiment studies to identify a limited but robust set of descriptors to predict NEMS contact performance for arbitrary material systems. To do this, we will identify the most important contaminants in relevant packaging environments. Then, we will examine the behavior of these contaminants between different material pairs to broaden the array of possible solutions which can then be screened. **For contact material development**, we will: (i) fabricate $Pt_xSi$ AFM probes and perform switching tests using a novel high-throughput test methodology; (ii) produce AFM probes of other contact material candidates we identify, such as Ru or $RuO_2$, and evaluate their cycling performance; (iii) fabricate and test an *in situ* SEM heater and observe the formation and release of candidate materials including $Pt_xSi$. **For the *ab initio* studies**, we will: (i) test the formation mechanism first on common surface materials including Pd, Au and Cu to finalize the identification of the descriptors; (ii) test the validity of our descriptors on existing materials, such as $Pt_xSi$, $RuO_2$ and available material for NEMS switches so far; (iii) apply our method to discover TP-immune materials; and (iv) provide support to the other thrusts to understand the mechanisms of TP formation, and develop even better approaches to enhance TP formation. **For the MD studies,** this involves: (i) manipulating the interactions between TP molecules to control the surface tension, viscosity and adhesion of small molecules and polymers; (ii) examining the effect of these conditions on the morphology of TP film and contact forces in MD simulation; (iii) collaborating with the *ab initio* modelers to develop a model for the growth of TP and its inhibition by oxygen gas; and (iv) establishing correlations between simulation results and AFM measurements. **For the microswitches**, we will determine and eliminate remaining failure mechanisms in promising materials. For example $RuO_2$ has high immunity to contaminants, but exhibits brittle failure. We will also investigate new materials on these contacts suggested by the theoretical efforts. **For NEMS development**, the goals will be to: (i) complete the design and fabrication of the third relay geometry; (ii) identify and design test structures in which to incorporate a selected set of contact materials.

## Broader impacts

If successful, we will discover new materials and operating conditions that make NEMS switches a viable technology for future low-power computers and portable devices. This has potential to save large amounts of energy worldwide. This work will also help maintain U.S. competitiveness in information technology by continuing technological progress in a key economic sector. Students conducting research in our labs will develop skills to lead future research in energy-efficient nanodevices, materials science, and tribology. Undergraduate students will benefit from a unique dual-institution summer internship exchange that will be implemented, and team-taught short-courses at conferences will broadly disseminate insights from these innovations.

## Data Management and Open Access

All of our findings, including the database of material systems we create and the experimental and modeling methodologies we develop, will be widely disseminated through research articles and conference presentations. Further, we will share our material systems database through a web interface hosted on a wiki-based website that we call *NEMSMatWiki*, to be developed next year. This wiki will be searchable and updatable by others, creating a community of knowledge-sharing researchers seeking the common goal of reliable NEMS devices.

## Publications

*Published, peer-reviewed journal publications*

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2. U. Zaghloul, and G. Piazza, *Highly scalable NEMS relays with stress-tuned switching voltage using piezoelectric buckling actuators*, IEEE Transactions on Electron Devices, **61**, 3520 (2014).
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4. U. Zaghloul, and G. Piazza, *Sub-1-Volt piezoelectric nanoelectromechanical relays with milliVolt switching capability*, IEEE Electron Device Letters, **35**, 669 (2014).
5. F. Streller, G. E. Wabiszewski, F. Mangolini, G. Feng, and R. W. Carpick, *Tunable, Source-controlled Formation of Platinum Silicides and Nanogaps from Thin Precursor Films,* Advanced Materials Interfaces, **1**, 1300120 (2014).
6. V. Brand and M. P. de Boer, *Oxygen-induced graphitization of amorphous carbon deposit on ohmic switch contacts improves their electrical conductivity and protects them from wear*, Journal of Micromechanics and Microengineering, **24**, 095029 (2014).
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8. F. Streller, G. E. Wabiszewksi, F. Mangolini, G. Feng, and R. W. Carpick, *Tunable, source-controlled formation of platinum silicides and nanogaps from thin precursor films*, Advanced Materials Interfaces, **1**, 1300120 (2014).
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*Conference publications*

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4. V. Brand, M. S. Baker, and M. P. de Boer, *Controlling environment and contact materials to optimize ohmic microrelay lifetimes*, in MRS Proceedings, mrsf13-1659-xx07-03 (2014).
5. V. Brand and M. P. de Boer, *Understanding contaminant-induced degradation in ohmic micro and nanoswitches*, Society of Experimental Mechanics Annual Meeting, Greenville, SC, June, 2014.

*Provisional patent application*

1. *Methods, apparatuses, and systems for piezoelectric nanoelectromechanical relays*, G. Piazza and U. Zaghloul.

# Controlling Hierarchical Nanostructures in Conjugated Polymers

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**Keywords:** polymer, processing, electronic structure, morphology

## Project Scope

Semiconducting polymers have achieved impressive benchmarks of performance.[1–3] However, predictive control of morphology through tailored processing methods and molecular structure would lead to further major advances. We are designing semiconducting polymers which form solution-phase assemblies that lead to solids with hierarchical 3D transport pathways (Figure 1).[4,5] The design of processing conditions will be enabled by efficient computational methodologies developed using experimental inputs. The development of scalable models to understand the role of domain boundaries in charge transport using high resolution electron microscopy of the hierarchical nanostructure will be key. These models will provide feedback to design next generation materials and guide the synthetic efforts, validating this methodology.

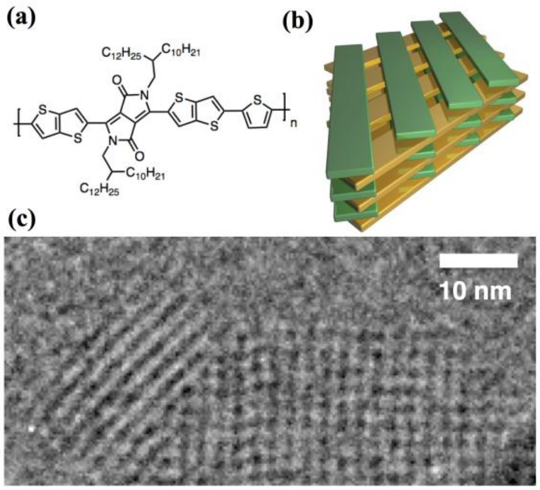

**Figure 1.** Charge transport in semiconducting polymers is limited by interchain electronic coupling. High performance semiconducting polymers such as **(a)** DPPTT-T have stiff linear backbones that can lead to expitaxial chain overlaps shown in **(b)**. **(c)** High resolution transmission electron microscopy reveals preferred molecular overlaps defined by the backbone structure.

## Relevance to MGI

Our research team has complementary expertise in computation (**Ganapathysubramanian**), physical characterization (**Chabinyc**), and synthesis (**Hawker**). We will accelerate our ability to discover new printable semiconductors by synthesizing model polymers to provide benchmarking data for development of codes that can predict conditions for the formation of controlled morphologies. These codes, in turn, will be used to predict the behavior of new materials reducing the design space. Our research effort will develop open source codes for modeling processing effects on morphology and provide open access structural datasets, such as high resolution maps of nanostructures in semiconducting polymers, for the materials research community.

## Technical Progress

We have begun initial steps towards coupling molecular design with computational methodologies to follow structure formation during coating flows. **Hawker** has designed new monomers that will enable complex hierarchical transport pathways and synthesis of initial generation materials is underway. To gain critical information on the size and shape of aggregates of semiconducting polymers as inputs for computational models of coating flows, **Chabinyc** is acquiring small angle x-ray scattering for a set of structurally diverse materials. **Ganapathysubramanian** has made progress towards a massively parallel in space-time framework for solving time-dependent non-linear diffusion equations that is essential for understanding coating flows.[6]

During the first months of the award, the PIs have also made plans to develop an initial graph theory based model to examine charge transport pathways determined by high resolution transmission electron microscopy. This initial work will use high resolution images of polymers that show preferential chain crossings set by their backbone structure obtained by **Chabinyc.**

### Future Plans

*Modeling process-structure physics:* In the next year, **Ganapathysubramanian** will work towards formulating *a posteriori* error indicators for the space-time formulations for the Cahn-Hilliard equations, as well as the Allen-Cahn equations. Furthermore, his group will develop and implement a unified framework for shear- and solvent evaporation- induced morphology evolution with crystallization based on the Allen-Cahn equations. Preliminary tests of these methods with experimentally determined inputs from **Chabinyc** and **Hawker,** such as molecular diffusivities (using gradient NMR methods) and aggregate size and shape, will help us progress towards validation (specifically trends of morphology metrics as a function of processing).

*Exploring structure-transport physics:* We plan to leverage and extend graph theory based models to explore the multi-scale nature of charge transport pathways in materials synthesized by **Hawker**. This will enable a hierarchical multi-scale characterization of high resolution transmission electron microscopy imaging performed by the **Chabinyc** group. Following this characterization, we anticipate performing full-scale (morphology aware) drift-diffusion analysis of these morphologies.

### Broader impacts

The development of new semiconducting materials and represents an excellent opportunity to train students across disciplines. Graduate student researchers will work in multidisciplinary research teams that combine computational analysis, synthesis, and physical measurement. The research will address a growing need for researchers with not only depth of knowledge, but also the ability to communicate across disciplines. A female graduate student researcher studying the physical morphology of polymers is being mentored by **Chabinyc** and **Hawker** on the project already.

PIs at both ISU and UCSB will leverage established strong links with local, minority-serving institution and organizations (i.e. **Ganapathysubramanian** is the faculty coordinator for the Women in Mechanical Engineering (WiME) program at ISU and **Hawker** is the faculty mentor for the UCSB Graduate Students for Diversity in Science (GSDS) group). **Chabinyc** and **Hawker** plan to engage promising Latino students from the diverse population at UCSB (22% Latino undergraduates) and via the Partnership for Research and Education in Materials (PREM) grants with the University of Texas, El Paso. **Ganapathysubramanian**, a member of the NSF REU site hosted by Mechanical Engineering at ISU and the DOE SULI program, will continue to leverage these two resources to provide research opportunities for community college students and minority serving institutions (Savannah State University, U Puerto Rico, Mayaguez).

### Data Management and Open Access

We will manage both experimental data and codes for computation. When codes and physical datasets are at and advanced stage, they will be made publically available to the research community by websites hosted at Iowa State University. We will also develop a public access format to store high resolution electron microscopy images of nanostructures in semiconducting polymers.

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## Publications

None.

# Computational Design, Rapid Processing and Characterization of Multiclass Materials from Genomic Ti-B-X Platform

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**Keywords:** Multiclass materials, Titanium boride, composite, cermet, ceramic, phase diagram

## Project Scope

This research is focused on iterative design, processing and characterization to gather the genomic data for specific material systems based on ternary Ti-B-X (X=Fe/Mo/Nb) alloy compositions. Using computational calculations and the understanding of the phase stability, alloying, and solute partitioning of the X element between the metal and boride phases, as well as the electronic structure and properties of ternary borides, a rich fundamental knowledge base of genomic material data will be created for Ti-B-X to simultaneously benefit material design in three material classes: metal-matrix composites, cermets and ceramics.

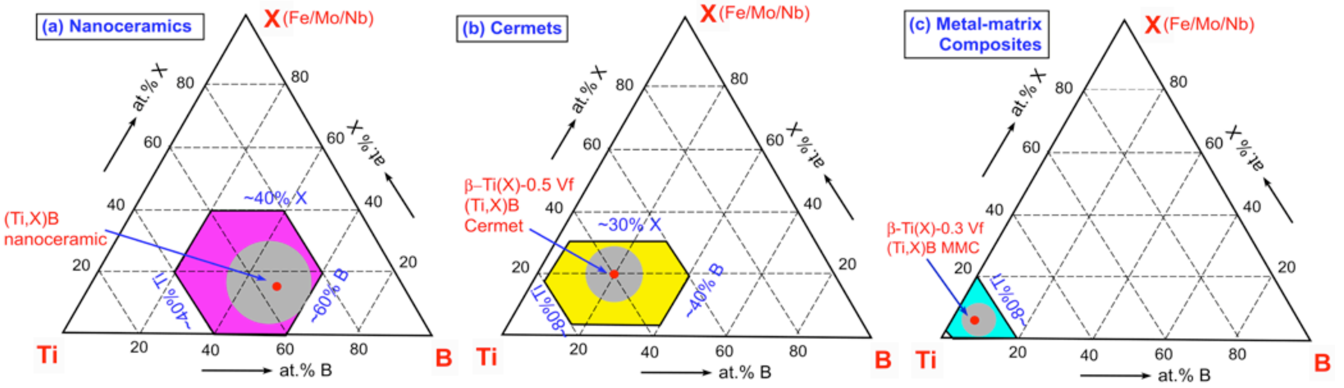

Figure 1. Compositions focused in the Ti-B-X system for material designs in three distinct material classes

## Relevance to MGI

The team will perform computational design, electric-field-activated synthesis and application-specific characterization of three material classes (ceramic, cermet and metal-matrix composite (MMC)) emerging from the Ti-B-X system as a platform. The proposal focuses on core research themes which simultaneously benefit these distinct material classes, leading to much greater impact on technological advances and on industry, in contrast to traditional design approaches focusing on a single material class or composition. The team will iterate through material design, rapid synthesis, and standard and application-focused characterization to uncover the genome of this material system and to benchmark its properties against contemporary advanced materials.

## Technical Progress

Progress is being made on three fronts: (i) initial composition selections for the Ti-B-X material classes are made by assembly of limited ternary phase diagram data and to identify regions for CALPHAD type calculations (ii) design and preliminary evaluation of rapid processing system and (iii) formation of an industry advisory panel. Composition domains for multiclass materials in Ti-B-X have been identified by synthesizing information of binary Ti-X systems and B-X systems. These will be the focus of CALPHAD calculation to establish phase domains and processing windows. We are currently building a pulsed-DC electric-field-activated sintering unit in cooperation with GTAT, Santa Rosa, CA. The new equipment will be installed in early 2015 to facilitate the rapid processing of material designs.

## Future Plans

This research will develop the Ti-B-X system as a platform for three distinct material classes (Figure 1), each having a range of uses. 1) Nanostructured ceramics based on (Ti,X)B rich compositions (volume fraction, $V_f > 0.98$ for hard boride phase) provide a locus for a new class of high-performance ceramics for wear-resistant bodies like ball/roller bearings, biomedical implants, nozzles, etc. 2) MMC compositions with low volume fractions of boride whiskers ($V_f \sim 0.1$-$0.3$) and with a large amount of tough, ductile phase show great potential to replace high strength steels (HSSs) for lightweight aerospace and automotive applications. 3) Compositions with intermediate boride content ($V_f \sim 0.6$-$0.9$) are essentially cermets that could serve as cutting, shaping and forming tools to compete economically with expensive WC-Co cermets.

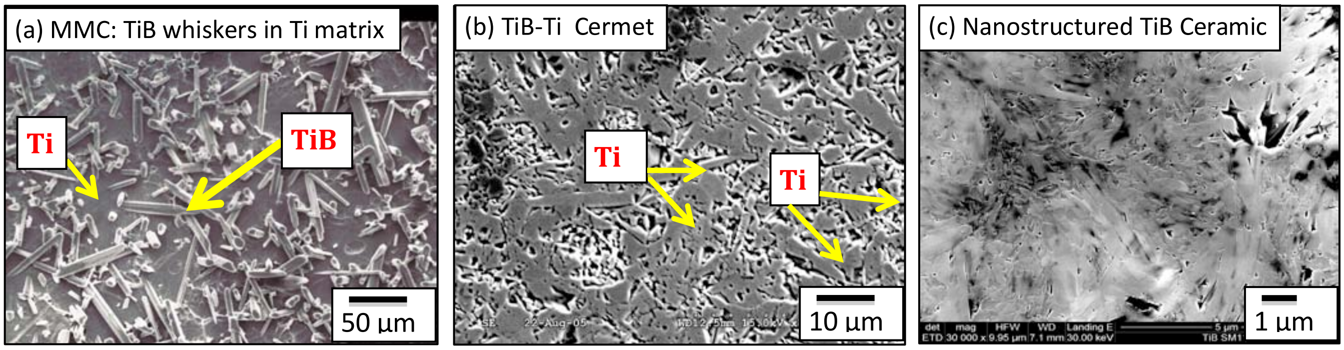

Figure 2. Prior work on binary Ti-B system: (a) Ti MMC containing isolated TiB whiskers (~24% TiB)[i], (b) TiB-Ti cermet (~90% TiB) containing alpha-Ti metal phase[ii], (c) Dense pack of high aspect ratio TiB whiskers forming bulk nanostructured TiB ceramic (~98% TiB) by reaction in solid state as documented in our work[iii].

The goal of this proposal is therefore to uncover the full genome of the Ti-B-X system while developing an iterative design approach that achieves increases in hardness, strength, wear resistance and toughness. It is hypothesized that: (i) the hardness and modulus of the binary boride phase, TiB, can be increased ($Hv > 2500$ kg/mm$^2$ and $E > 500$ GPa) by designing on the basis of ternary compositions, Ti-B-X, (X = Fe/Mo/Nb), to form isostructural ternary borides (Ti,X)B; and (ii) the ductility and toughness of the Ti matrix can be engineered (>10% Elong.) by stabilizing the BCC beta phase by solid-solution formation in Ti by the same elements.

### Broader impact (Optional for DOE grants/FWPs)

A. Advancing New Materials Design Data and Technology: First, in (Ti,X)B ceramics, the goal is to achieve high hardness of the dominant ($V_f \sim 0.98$) boride phase by doping with X while also enhancing the ductility of residual titanium. Second, in MMCs, the ductility of the matrix beta-Ti will be enhanced to compete with HSSs. Third, the design of cermets with intermediate proportions of Ti(X) matrix and (Ti,X)B reinforcement phases will fit naturally between the two extremes represented by ceramics and MMCs.

B. Advancing Education Opportunities: The funding will support one post-doctoral researcher, several graduate students at UofU and at UIUC. At UIUC, PI Trinkle will be engaged in training and developing high school science teachers to expand science education in the city, and to develop valuable connections for identifying talented minority students to recruit to UIUC.

C. Advancing Commercialization Opportunities: The potential to commercialize specific outcomes of the research will be enhanced by: 1) the rapid, iterative materials design strategy that culminates in application-centered testing; 2) the GOALI participation of an industry member in the academic research, as well as the related Industry Advisory Panel; and 3) the transparent dissemination of broad-based material data which facilitates consideration of the Ti-B-X system by the potential adopters in industry.

### Data Management and Open Access

All computational data will be made available through the NIST MatDL project, where datasets are given unique digital object identifiers (hdl objects, in this case). This ensures that the data is publicly accessible.

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# Collaborative Research for the Design and Synthesis of Novel Magnetic Materials

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**Keywords:** genetic algorithm, density functional, magnets

## Project Scope

This collaborative research project implements new, transformative strategies for the design of novel magnetic materials, with special focus on sustainable materials containing earth-abundant and inexpensive elements. The project couples a strong *experimental effort* with recent *theoretical* advances in quantum modeling algorithms and software, data-mining techniques, and high-performance hardware to accomplish its objectives. Magnets play a crucial role in contemporary technologies, and this research focuses on the discovery of new Fe-Co-X phases with anisotropic structures, high magnetization, high Curie temperatures, high spin polarization and high magnetic anisotropy.

## Relevance to MGI

The technical design and synthesis of new magnetic materials is a formidable problem, especially so given the myriads of possible combinations of composition and structure. This research uses computationally driven phase-diagram explorations and materials-structure prediction coupled with experiment to identify materials with desirable properties for magnetic applications. A new adaptive genetic algorithm coupled to first-principle codes is used for structure and property searches. The algorithm possesses the speed and efficiency of classical simulations, while maintaining the accuracy of quantum-based simulations. Concurrent, experimental research involves novel synthetic techniques and a comprehensive set of characterization methods.

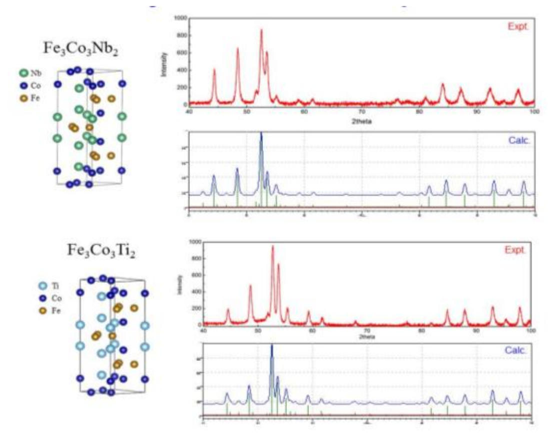

**Figure 1.** Preliminary results on new compounds $Fe_3Co_3Nb_2$ and $Fe_3Co_3Ti_2$. Co Kα x-ray diffraction patterns are shown in red, and calculated patterns from AGA derived structures are shown in blue.

## Technical Progress

Initial work has been focused on improving the speed of the real-space *density-functional-theory* (DFT) code. In addition, we have obtained preliminary *adaptive genetic algorithm* (AGA) results on new metallic compounds of the form $Fe_3Co_3Nb_2$ and $Fe_3Co_3Ti_2$. These compounds have been synthesized by rapid quenching and their x-ray diffraction patterns are shown in Fig. 1. The AGA method has been employed to search for ground-state structures and two low-energy structures with space group 174 (P-6) are shown in Fig. 1 along with calculated diffraction patterns. The agreement with experiment is good with some discrepancies (for $Fe_3Co_3Nb_2$) at higher angles. The magnetic properties of these compounds including $M_s$, $T_c$ and anisotropy constant are being investigated.

## Future Plans

We will perform computational phase-diagram exploration and materials-structure prediction to identify candidate chemical compositions and structures that have desirable properties for permanent-magnet applications. Structures of the nanoparticles and crystals will be predicted at the atomic level using a genetic algorithm with first-principles density functional calculations for the energy and properties evaluations. The first-principles *adaptive genetic algorithm* (AGA) developed at Iowa State University [1] will be used for structure searches. This AGA algorithm will be integrated with the real-space pseudopotential-density functional code, called PARSEC [2], developed at the University of Texas at Austin. This is expected to result in a highly efficient code for structural searches. Machine learning techniques will also be employed to study the correlations between the structures and the magnetic properties and to improve the AGA performance. Based on the low-energy structures obtained from the AGA search, we will employ cluster expansion techniques to expand the search for a larger number of atoms. The cluster expansion calculation will also be coupled with Monte Carlo simulations using the Wang-Landau algorithm for free-energy calculations in order to explore the alloy phase diagrams as the function of composition and temperature.

The experimental synthesis methods will include cluster synthesis with an inert-gas-aggregation, cluster-deposition system [3] as well as a rapid-quenching or melt-spinning system. The cluster deposition system produces monodispersed particles of controlled size ranging from about 1 nm to 20 nm. Typically the rms size distribution ratio is $\sigma/d \approx 0.10$ where $d$ is the average diameter. $\sigma/d$ can be reduced to about 0.03 if a quadrupole mass selector is used.

## Broader Impact

Our multicomponent broader-impact activities will center on the following efforts: (1) Graduate Education and Training, (2) Summer Intern Program, (3) Alice in Wonderland Program, (4) Nanocamp and STEM After-School Programs.

## Data Management and Open Access

A notable aspect of our work will be to emphasize informatics and data-mining techniques as a means to unravel important properties of magnetic materials and to analyze existing databases. In its simplest form data mining exploits underlying low-dimensional representations inherent in large data sets. Datasets that have many representatives of different types of objects are necessarily correlated and the correlations between different representatives can be exploited. For example, a question which can be answered by mining datasets of materials may be: Which compound is the most likely to have a certain property among a group? This can be guessed by establishing a distance between the compounds and then a neighborhood graph. We will apply machine learning techniques to search among Fe-based and Co-based binary alloys, those that have certain desirable characteristics. To do this we will exploit our computational codes for performing calculations to extract the features required for the analysis.

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## Publications

Nothing to report.

# Collaboration to Accelerate the Discovery of New Alloys for Additive Manufacturing

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**Keywords:** Additive Manufacturing, Solidification, Microstructure, Viscoplastic properties, Data Science.

### Project Scope

This project seeks to design a new β-titanium alloy that exploits the unusual characteristics of additive manufacturing (AM) using data-driven design. It integrates high-throughput combinatorial techniques, state-of-the-art materials characterization, computational methods, and data-science to: (1) discover and model the interrelationships between the alloy composition, the far-from equilibrium conditions of AM processes, and the resulting microstructure and properties; (2) describe key materials attributes using multi-dimensional, multi-spatial, and multi-spectral approaches; (3) determine hidden mechanisms between composition, structure, and properties using data science approaches; (4) validate mechanisms via computational modeling and critical experimentation; and (5) *design* a new material *for* AM.

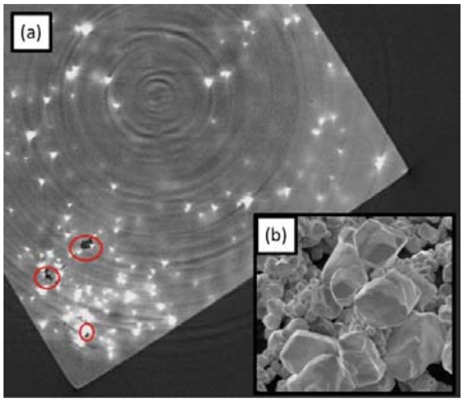

**Figure.** (a) High Energy CT of AM Ti-W, illustrating both pores (circled) and bright unmelted W (see **b**), illustrating the distribution of particles in the liquid state.

### Relevance to MGI

The activities of this multi-university project are intimately coupled. In addition to regular technical exchanges and data sharing, the project also includes themed summer workshops on “Discovery Integration” and “Statistical Validation”. Also, as the project seeks to provide *tools*, a series of “industrial dissemination” workshops will be held where companies focused on the implementation of AM will be informed of progress being made on the project, including both models, data, and materials discovery.

### Technical Progress

This *new* project has some initial results. A Ti-xW gradient produced by Collins’ group using blends of elemental powder has been shared with Rollett’s group, who has obtained a first of its kind high energy x-ray computed tomography dataset of a single phase titanium alloy but which exhibits a multi-composition (i.e., multi average atomic number) *body centered cubic* (*bcc*) structure (shown in **figure**). This result has been obtained at the Advanced Photon Source, and demonstrates the possibility of eventually using a combination of CT and high-energy diffraction microscopy to resolve different average atomic numbers of the same crystal structure. The Ti has been stabilized in its *bcc* structure, but the material was processed in a manner to avoid complete dissolution of the *bcc* elemental W. In this experiment, it is possible to observe the relatively homogeneous distribution of the elemental *bcc* W – an important observation for this binary system, which exhibits an endothermic enthalpy of mixing, and thus less vigorous mixing of constituents in the liquid phase. This information is critical for not only multi-physics simulations of the temperature during deposition but also solidification modeling that will be conducted by Lesar’s research group. A compositionally graded specimen has been provided to Kalidindi for assessment using nanoindentation techniques. On the computational side, Lesar and his student have written a working parallel Lattice-Boltzmann fluid flow code while Collins has shared a basic physics-based constitutive model for Ti-64 with Rollett for inclusion in future crystal plasticity-FEM models.

**Future Plans**

As noted, the project integrates several activities, including: (1) high-throughput combinatorial materials synthesis using laser-based AM of β-stabilized Ti systems including various α-stabilizers, β-stabilizers, and dispersoid formers; (2) solidification modeling using the Lattice-Boltzmann model that will allow coupling of various compositions to the solidification studies (e.g., fluid velocity, temperature distributions/gradients, material/phase distributions, etc.), which will provide critical boundary conditions and new understanding of solidification for additive manufacturing across various compositions; (3) accelerated material property measurement using spherical nanoindentation studies to measure the properties of the phases present in the systems of interest; (4) materials characterization, including quantification/interpretation of texture and grain boundary character distributions of various systems for different processing conditions and the simultaneous establishment of 3D datasets for systems of interest; (5) establishment of a physical model for the influence of composition and microstructure on the mechanical properties of the additively manufactured specimens; (6) modeling of microstructural evolution under phase nucleation/grain growth/recrystallization using tools such as the Potts model and phase field model to understand how these materials respond to thermal treatments; (7) data-driven approaches to establishing processing-structure-property linkages to guide accelerated materials development efforts; and (8) the viscoplastic modeling of the materials. In the immediate future, the team will continue with activities #1-4. Ti-xE (E=Ta, Fe, W, Sn, C, Ge) binary systems will be produced using a variety of processing conditions. The resulting material will be heat-treated and shared amongst the team for subsequent microstructural and property characterization, providing key data for activities #5-8. Lesar will continue to develop the process model, incorporating heat flow, mass flow, and fluid convection. Rollett will develop synthetic (digital) microstructures with varying constituent phase properties to predict performance. Kalidindi will use data analytics to quantify how phase morphology/distribution change as a function of both thermal treatment and composition.

**Broader impact**

Critical to this project are the summer integration workshops and industrial dissemination workshops. Regarding the former, the PIs plan on summer exchanges amongst the institutions for specific activities. For example, it is essential that those students working on #1 (high-throughput materials synthesis) and #2 (solidification modeling) spend time understanding the details of each activity to not only promote knowledge sharing but also to better educate the future materials researchers and scientists on both experimental and computational tools. Regarding the *industrial dissemination workshops*, the team will share openly the details of the methods, data, results, and any performance metrics of a newly designed alloy with industrial partners pursuing AM (i.e., OEMs, their supply chain) so that they can leverage the tools and the materials discoveries, shortening their development cycle.

**Data Management and Open Access**

As described above, establishing highly productive cross-disciplinary, distributed, collaborations is one of the core activities of this project. This project will build on ongoing efforts in Kalidindi's research group at designing, creating, and launching an open science collaboration platform called MATIN. A critical functionality that has guided the MATIN development thus far is the need to track (i.e., version control and provenance) and keep together all the data, codes, and discussions with connected (i.e., graphed) persistent identifiers, while keeping a low maintenance cost for the sustained operation of the collaboration platform. Consequently, we embraced a strategy that provisioned existing web services (e.g., GitHub, Authorea, Plot.ly, Google+) for all the main functionalities of this platform. The digital recording of the code and data transformations that occur naturally among the users of this collaboration platform provides rich new data that can be mined for best integration practices and workflows in all the endeavors (including research, education, outreach, and knowledge transfer).

**References**

None.

**Publications**

As this project has only recently been initiated, there are not yet any publications resulting from this award.

# Inferring grain boundary properties from heterogeneous data

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**Keywords:** grain boundaries, networks, microstructure, Bayesian inference, localization.

### Project Scope

The goal of this project is to build analysis tools that infer accurate and general grain boundary (GB) crystallography-property relations with quantified uncertainty by assembling partial but complementary data readily obtainable with existing experimental and modeling methods. These tools will markedly enhance our ability to predict and control—through computational design—materials properties governed by GB networks, such as intergranular fracture, diffusion, and embrittlement. We have adopted gallium permeation through GB networks in Al—shown in Fig. 1—as a model problem on which to develop and validate these tools.

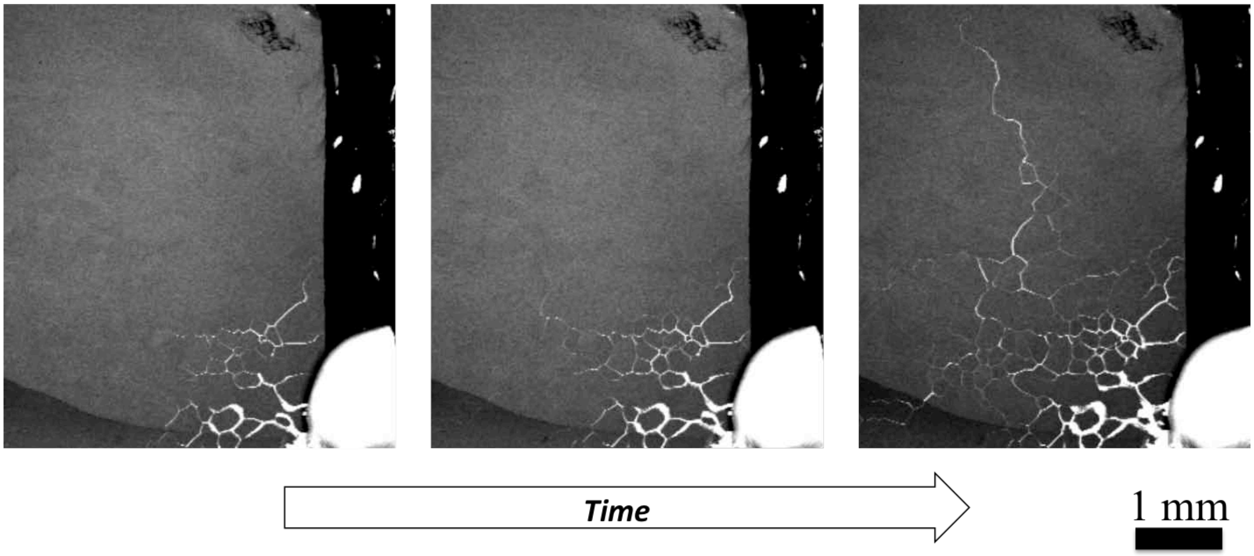

**Fig. 1:** Time-lapse sequence of an *in situ* Ga permeation experiment. The Ga reservoir is at the bottom right corner. Note the high diffusivity GB path that branches out from the initial cluster of wetted GBs in the last frame on the right.

### Relevance to MGI

The crux of this project is integration of information obtainable from easy-to-perform experiments and simulations. GB properties depend, at minimum, on five crystallographic variables. Conventional approaches, such as investigation of individual GBs using electron microscopy or atomistic modeling, provide incomplete information concerning GB crystallography-property relations. However, the information provided by many of these techniques are complementary. This project integrates information available from multiple sources using analytical techniques such as Bayesian inference and GB network analysis to obtain a more complete understanding of GB crystallography-property relations in a resource-efficient way.

### Technical Progress

We have selected Ga permeation into Al GBs as a model problem because this process is rapid and easy to observe, allowing us to perform high-throughput experiments. We developed methods to track Ga permeation *in* *situ* in a scanning electron microscope (SEM) using backscattered electron (BSE) imaging and to relate them to the full five-parameter GB character, obtained through two correlated electron backscatter diffraction (EBSD) measurements. Fig. 1 shows that within a single permeation experiment, we can distinguish between high diffusivity paths as well as clusters of GBs that are either not permeated at all or at a much slower rate. These experiments give qualitative insights into GB crystallography-property relations for Ga permeation into Al, e.g. that Ga permeation velocity does not scale with GB misorientation angle for high angle, general GBs.

To infer quantitative GB crystallography-property relations from experiments such as that shown above, we have made theoretical advances in the complementary tasks of homogenization (calculating aggregate properties from GB behavior) and localization (calculating GB properties from aggregate behavior). Specifically, we studied how to infer GB diffusivities from the diffusivity of the polycrystalline aggregate ($D_{eff}$). We demonstrated that the Generalized Effective Medium (GEM) homogenization scheme provides quantitatively accurate predictions of $D_{eff}$ in GB networks with diffusivity contrast ratios from 10 to $10^8$. We then solved the inverse problem of localization by deducing the local diffusivity of each boundary with given microstructure data and measurements of $D_{eff}$ from simulations. These advances are underpinned by an improved ability to properly represent GB networks in polycrystals. Spectral representations of triple junction distribution functions in GB networks provide a mathematical connection between crystallographic texture and the structure of grain boundary networks. Building on this work, a mathematical framework to define the triple junction hull was formulated, which describes the space of all physically realizable triple junction distribution functions. These results are crucial to improving the homogenization and localization schemes used so far. They also show the extent to which grain boundary networks might be designed through the control of crystallographic texture alone [1,3,4].

Finally, we are integrating macro-scale measurements on GB networks, such as those shown above, with atomistic [2] and mesoscale [5] simulations as well as data available in the literature. To this end, we use Bayesian inference. This approach requires a “likelihood model” that predicts the probability of observing a specific Ga permeation rate provided that a given permeation mechanism holds. We formulate this permeation model using the phase field method. GBs are modeled as surfaces with non-uniform energy distributions and Ga concentration in a GB is described using an order parameter that obeys the Cahn-Hilliard equation. By modifying the gradient energy penalty parameter in this equation, we describe permeation mechanism ranging from Fickian diffusion to front propagation. We demonstrated the efficacy of our model as well as a first application of Bayesian inference to it on the model problem of inferring the properties of a patterned substrate from the behavior of a film deposited on the substrate [5].

### Future Plans

In follow-on work, the tools developed within this project will be applied to infer the dependence on GB crystallography of GB properties such as fracture toughness, susceptibility to sensitization, and H solubility.

### Broader impact (Optional for DOE grants/FWPs)

This project promotes MGI workforce development by supporting two full-time graduate students and two part-time postdoctoral researchers. These individuals are mastering and innovating tools that bridge traditional materials science and data analysis disciplines. They are poised to become MGI thought leaders as they transition to new roles as independent researchers.

### Data Management and Open Access

Data and codes created within this project will be made available on through MIT’s archiving service DSpace@MIT. All preserved data will be attributed to the researcher who produced it, but no private, confidential, or classified information will be stored. All preserved data will be associated with the appropriate metadata, which will describe how content should be accessed and interpreted.

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# Multifunctional Interfacial Materials by Design

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**Keywords:** Heterointerfaces. Thin Films, Multifunctional Oxides, Heteroepitaxy

## Project Scope

Complex oxides and the interfaces between them create juxtapositions between different symmetries and ordered states. These are some of the most promising materials in which to realize new phenomena that will challenge our current understanding of materials, and that will develop new electronic device directions that address our society's technology needs. Our project focuses on an iterative cooperation between forefront theory and experiment that determines the fundamental principles controlling new physical phenomena in oxide thin films and heterostructures. We use these principles to generate new functionalities, and synthesize and investigate designed materials for novel electronic devices.

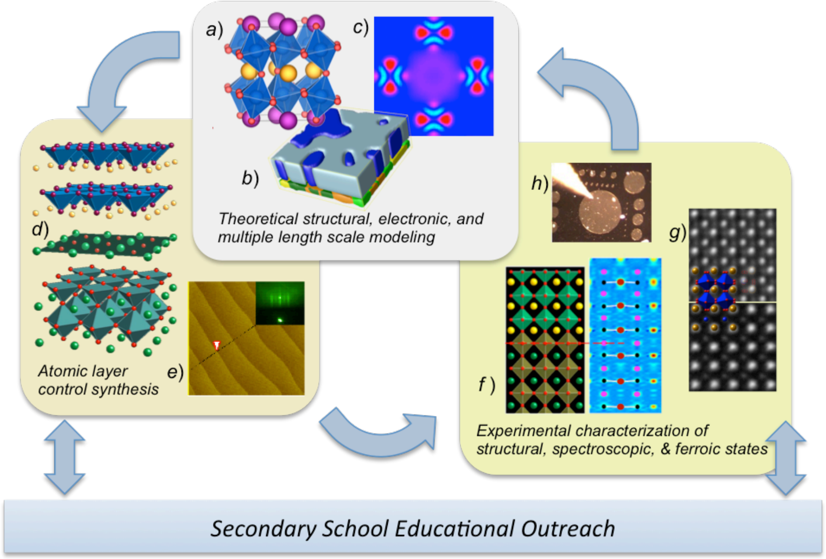

Figure 1: counterclockwise from top: **Theoretical Modeling**, showing *a*) octahedral rotations generating ferroelectricity, *b*) ferroelectric domain structure of a $(SrTiO_3)_4/(BaTiO_3)_8$ superlattice, *c*) oxide interfacial charge density; **Interface Synthesis**, showing *d*) layer by layer growth *e*) AFM/RHEED pattern of epitaxial growth; **Characterization**, showing *f*) Synchrotron reconstruction of interface structure *g*) TEM analysis of oxygen displacements *h*) low-temperature probe of ferroic state.

## Relevance to MGI

We have integrated iterative feedback loops in all stages of the research. T the complex nature of multicomponent oxide materials and interfaces requires a first step of theory and modeling to identify promising directions. This includes first-principles calculations of electronic structure, phenomenological theory of structural properties and phase stability, and phase field modeling of mesoscopic properties. Synthesis is quite challenging, and incorporates feedback loops of in-situ RHEED, and ex-situ x-ray diffraction and scanning probe microscopy, basic evaluation of electrical and magnetic properties, and finally detailed experimental properties measurements, which directly feeds back to theory. Examples of particular systems are detailed in the next section.

## Technical Progress

We have made significant progress in understanding and developing several fundamental components of complex oxide thin films and heterostructures. Many of these involve oxide materials in the (111) orientation, which we have found to require the MGI feedback process for successful synthesis and development. Through theoretically inspired geometric design relying on thin-film epitaxy, we have converted bulk centrosymmetric $NdNiO_3$ to a polar structure with inversion symmetry breaking. We find this to be particular to the (111) orientation, and not possible in 100 oriented films. This design takes advantage of strong electronic and structural correlations in $NdNiO_3$ films, and opens avenues for engineering new material systems with multi-functionality. The graphene-like structure of 111 $SrIrO_3$ is predicted theoretically to support topological states at surfaces and interfaces. Although extremely challenging to grow, we have successfully synthesized ultra-thin films with extensive feedback from lab and synchrotron based structural characterization. The (111) orientation of $LaAlO_3$ / $SrTiO_3$ heterointerfaces supports a two-dimensional electron gas whose properties depend on the unique interfacial characteristics in the (111) orientation. Theory offers two different predictions of these properties, with feedback from synthesis and experimental measurement providing the key information, that structural reconstruction is replaced by an electronic version, with bonding across the interface resulting in electronic characteristics unique to the (111) orientation. Synthesis also relied critically on feedback from synchrotron-based evaluation, transmission electron microscopy, and variable temperature electrical and magnetic properties. The bulk form of piezoelectric material PMN-PT is uniquely positioned as one with dramatically large piezoelectric response. Thin-films can provide these functionalities in next generation devices including nanoscale MEMs, sensors, and electronic devices relying on strain-dependent materials. But interaction with the substrate can dramatically alter the piezoelectric properties, shifting the morphotrophic phase boundary, and changing the electric-field dependence of the piezoelectric properties. With feedback loops from phase-field modeling, direct interferometric determination of thin film surface displacements, and structural analysis with transmission electronic microscopy, we have synthesized and optimized PMN-PT thin films with giant piezo response. We have also developed a technique to synthesize free-standing PMN-PT thin films to provide additional feedback to theory by a direct evaluation of the substrate strain effect.

### Future Plans

Our accomplishments demonstrate that the MGI feedback loop procedure is essential to continued progress in complex oxide thin films and heterostructures in all aspects of the research, including theory, synthesis, and experimental measurement. The delicate balance of structural deformations, electronic correlations, and interfacial interactions in complex oxides precludes the traditional approach to development and implementation. Some of our most promising results have come from films and heterostructures in the (111) crystallographic orientation, which we have found to provide a landscape in which this balance can lead to unexpected and technologically useful phenomena. Our future plans are to use the feedback procedure, and the insights we have discovered through the MGI program, to identify new complex oxide systems and heterostructures with similar balances and opportunities. A final goal is a rationalization of this procedure, identifying key structural and electronic building blocks that will make the process available to the broader community.

### Broader impact (Optional for DOE grants/FWPs)

All students have been co-advised by the team faculty. Research students have spent time working in the different laboratories of the UW-Madison PIs, familiarizing the students with various research areas using forefront research facilities, and foster a multidisciplinary viewpoint, preparing the student to adapt to emerging technologies. Several have developed further breadth with visits to Argonne National Laboratory and work at the Advance Photon Source. We have had regular thrust meetings of the team using videoconferencing, with extensive student participation. We have held two workshops, including MGI PIs, students, and postdocs, as well as selected external collaborators. These included student presentations, as well as technical rump sessions, in which students can better understand the process of developing and maintaining successful research programs.

### Data Management and Open Access

Interfacial oxide modeling parameters will be made available in an open-access repository. Free-of-charge account generation and log-in will be required for access to the database.

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# Discovery and Design of Ferromagnetic Shape Memory Alloys by Quantum Mechanical Simulation and Experiment

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**Keywords:** Shape memory alloys, metamagnetic materials, magnetocaloric effect, phase transitions

## Project Scope

Our program is centered on predicting, designing, and optimizing shape memory alloys exhibiting the giant inverse magnetocaloric effect and/or the elastocaloric effect (changes in applied stress and/or magnetic field induce a change in the temperature). We focus on several material classes, including the Heusler alloys Ni-Mn-In, in which a phase transformation between a ferromagnetic austenite and a paramagnetic martensite induces the effect. Our goal is to design/identify several new materials exhibiting largest magnetocaloric/elastocaloric response measured. New theories/frameworks to be developed include phenomenological models of temperature dependent magnetic response, and frameworks to predict lattice and magnetic entropy changes.

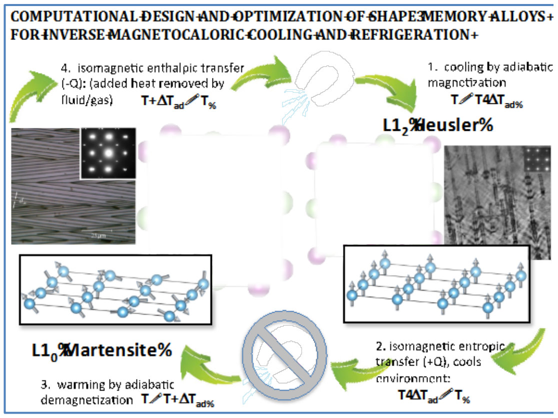

**Figure 1.** Schematic of solid state magnetic cooling via metamagnetic shape memory alloys.

## Relevance to MGI

Computation and experiment are tightly coupled to design and discover the most promising materials that (i) exhibit a giant magneto/elasto caloric response (ii) in a broad temperature range, with (iii) minimal hysteresis and (iv) minimal thermal-cycling induced degradation. Performance metrics are assessed by a combination of first-principles simulations and (newly developed) phenomenogical models to predict coupled stress/magnetism/temperature response. Targeted experiments on single crystal samples are being used to validate the computational models by studying the stress and/or magnetic field induced transition from the martensite phase to the austenite phase in selected compositions producing a significant change in magnetization.

## Technical Progress

We have built the computational framework for the calculation of the lattice contribution to the entropy. The current approach integrates existing first-principles codes[1] and the open-source software PHONOPY[2], with a house-developed set of routines for calculating the lattice entropy from the phonon spectrum. Currently, the lattice entropy framework is based on a quasi-harmonic description, although it may be expanded in the future. We are in the process of assessing the framework for $Ni_2FeGa$ and NiTi shape memory alloys. Experimentally, we have implemented the set up for stress/strain measurements, and have carried out stress/strain/temperature measurements for these two materials. The results have shown material dependent temperature changes, as expected due to the difference in entropy between the materials. The $Ni_2FeGa$ specimens had an average temperature drop of 7.6 °C for the [011] oriented crystal and 8.5 °C for the [001] oriented crystal. NiTi had a higher average temperature drop, 12.2 °C for the [148] oriented crystal and 13.2 °C for the [112] oriented crystal.

These two materials constitute our preliminary testing ground for coupled experimental/computational development, which will be expanded for large-scale, high-throughput calculations on many candidate materials.

## Future Plans

In the next phase (6 months), we will additionally implement the computational framework for the calculation of the magnetic contribution to the entropy. This includes developing and assessing models of the temperature-dependent magnetization. Correspondingly, we will build the experimental set up to carry out the stress/strain/temperature measurements in the presence of an applied magnetic field. Following this, the full computational framework will then be executed in a high-throughput manner to carry out lattice and magnetic entropy calculations within the class of traditional shape memory alloys (NiTi) and the Heusler-type metamagnetic shape memory alloys. Targeted single crystal experimental measurements will be used to assess/improve/validate the model.

## Broader impact (Optional for DOE grants/FWPs)

Magnetic cooling, in which a magnetic field is used to change the temperature of a material, offers a profoundly different energy solution to applications involving power generation, heating, and refrigeration. The research broader impact of this work is the identification of high-performance shape memory alloys for solid state cooling and refrigeration, and an assessment of the performance attainable within this class of materials. There are several educational broader impacts, including: training of graduate students, delivery of online seminars to the shape memory alloy community, and curriculum development. We will sponsor a half-day workshop on computational design methods, which will be integrated into a short course on metals regularly taught by co-PI Huseyin Sehitoglu. The methodology results of the work will be incorporated into a design activity for a weeklong residential summer camp held at Illinois to attract female high school students towards careers in engineering, for which PI Elif Ertekin is the director.

## Data Management and Open Access

All code development will be made available as fully open-source under the GNU General Public License (GPL) to enable others to freely incorporate, modify, use in future work, *etc.* subject to the requirement that any derivatives also be GPL licensed. Any codes/software will be made freely available for download via our professional websites. Source code is regularly archived using industry-standard compression formats; all raw data, graphs, images, videos generated are stored on redundant RAID5 in industry-standard digital electronic format (TIFF, PDF/EPS, AVI), and deposited to University of Illinois Library's IDEALS (Illinois Digital Environment for Access to Learning and Scholarship) campus digital repository. IDEALS provides preservation, search, and browsing functions compliant with all preservation and archiving standards. Metadata for project data is assigned in accordance with established standards and best practices (Dublin Core).

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# Advanced material based on atomically thin layered building blocks—iterative design based on chemistry and topology

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**Keywords**: Functionalized graphene, nanocomposites, mechanochemistry, bond-selective chemical transformation, load transfer.

**Project Scope**. This project aims to establish a paradigm shift in materials design by combining theory, modeling, and experimentation in a bottom-up approach to maximize the strength and toughness of functionalized graphene-based nanocomposite materials that emulate the performance of natural nacre. Specifically, we aim to optimize the use of graphene oxide (GO) sheets in nanocomposites through fundamental studies of the strength and stiffness of individual sheets as well as sheets that are connected together by crosslinking elements that maximize load transfer and performance. At the end of the project, we will develop a fundamental understanding of the roles that different interfaces and topological assembly play in modulating the mechanical behavior of nanocomposites based on GO.

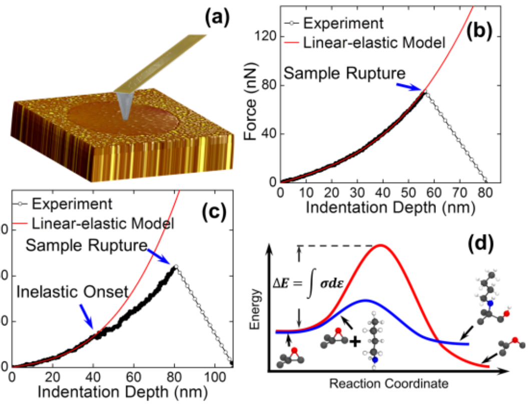

**Figure 1**. (**a**) Schematic of AFM nanoindentation test on a suspended circular GO membrane. (**b** and **c**) Typical brittle (b, minority) and ductile (c, majority) force vs. deflection depth curves for GO membranes. (**d**) Energy diagram comparing the reaction pathways for the mechanochemically induced C-C ring-opening of the epoxide group activated by strain energy (red) and the conventional C-O ring-opening by butylamine (blue).

**Relevance to MGI**. A close, iterative synthesis-measurement-modeling loop has been established in this project. Freestanding monolayer GO sheets were synthesized and assembled using Langmuir-Blodgett deposition. Then, nanomechanical experiments were carried out to investigate their mechanical properties (Figure 1a). Stimulated by the experimental findings, semi-empirical quantum mechanics models were developed to formulate a molecular-level understanding of the underline deformation mechanisms. With the feedbacks from both experiments and modeling, modifications to material synthesis methods were proposed to develop materials with novel properties.

**Technical Progress**. By combining nanomechanical experiments carried out with an atomic force microscope (AFM) and density-functional tight-binding calculations, we discovered a novel mechanochemically induced epoxide-to-ether functional group transformation in epoxide-rich GO monolayers. In the AFM nanoindentation experiments, the majority of the force vs. displacement responses of GO mainly exhibited a ductile failure mode that is in stark contrast to the catastrophic ruptures of pristine graphene and less-oxidized GO containing mainly hydroxyl groups. These responses followed the linear-elastic solution at the beginning of the indentation, but then deviated, indicating the inelastic deformation developed in the material (Figure 1c). Semi-empirical density functional based tight-binding (DFTB) calculations suggest that the “plasticity” of GO observed in these experiments can be attributed to novel mechanochemically induced epoxide-to-ether group transformations. The activation stresses obtained by MM and MD calculations also agree reasonably well with the measurements. Further supporting these conclusions is the observation that butylamine-modified graphene oxide (A-GO), which has a minimum amount of epoxides, has significantly reduced “plasticity” compared to original GO.

To explore the behavior and properties of functionalized graphitic interfaces that exhibit hydrogen bonding, we also conducted *in situ* peeling tests inside a scanning electron microscope (SEM). Multiwalled carbon nanotubes (CNTs) coated with propionic acid functional groups were peeled away from highly ordered pyrolytic graphite (HOPG) coated with the same functional groups. The adhesive energy of the functionalized surfaces was found to be in the 1.45-2.36 J/m$^2$ range, approximately one order of magnitude higher than that between pristine graphene surfaces and suggest that hydrogen bonding can play an important role in load transfer.

Through coarse-grained molecular dynamics (CGMD) simulations on layer-by-layer graphene-polymer nanocomposite structures, we have also shown that confining the polymer layer to nanoscale dimensions can significantly alter the mechanical response of the graphene nanosheets, giving rise to elastic properties that are a function of material geometry as well as bulk material properties. The topological constraint by the hard graphene phase induces strong anisotropy in the system by aligning the polymer chains parallel to the interface. Consequently, the in-plane elastic modulus becomes dramatically higher when the polymer layer thickness is in the order of the radius of gyration ($R_g$) of bulk polymer. These results explain recent experimental observations that suggest orders of magnitude differences in the mechanical properties of the native and extracted states in nacre and serve as a guideline for designing nacre-mimic nanocomposites with optimized elastic properties.

**Future Plans**. Thin films of GO composite will be fabricated by introducing a soft matrix material (such as polyvinyl alcohol (PVA), a block copolymer, or a protein) between two GO monolayers. AFM nanoindentation tests will be used to measure elastic modulus and damage stress of this sandwich system as parameters such as polymer length and matrix thickness are varied. The resulting data will allow us to relate the interfacial interactions in GO-based composites with their mechanical properties and behavior. We will then vary the matrix material to identify the structure and chemical functionalizations that yield optimal mechanical properties.

In the peeling study, we plan to investigate the surface energy between graphene oxide sheets as a function of the environment, e.g., humidity and temperature using nanomechanical experiments. We will also develop molecular mechanics models validated by the experiments to study the adhesion mechanism. The outcome from this study will provide us with valuable insights to guide the size-scaling of the GO properties.

We will study the fracture toughness of graphene-polymer nanocomposites by developing models that can explain the effect of physical confinement on both elastic response and toughness of polymers in nacre-mimic nanomaterials, thus providing guidelines for optimizing their mechanical properties. We will also extend our CGMD studies to GO-based nanocomposites, where the polymer phase can play even more important role in the overall mechanical properties to compensate for the lower in-plane elastic modulus of GO.

**Broader impact (Optional for DOE grants/FWPs)**. This project has supported the training of graduate students Lily Mao, Zhaoxu Meng, Michael Roenbeck, Rafael Soler-Crespo, and Wenjie Xia. In addition, it has helped the professional development of Drs. Luis Ruiz, Chen Shao, and Xiaoding Wei by involving them with project/team-management tasks and honing their mentoring skills as senior lab mentors to these students.

Lily, Rafael, and Michael have engaged the community by participating in several outreach activities. Lily is serving as a tutor to local underrepresented-minority middle and high school students through NU’s Project EXCITE and Northwestern-Lincolnwood Science Outreach Program. Rafael and Michael assisted the Evanston-based association *Jugando con la Ciencia*, which seeks to promote scientific education to Latino children, by explaining the roles of chemical and mechanical engineers and helping children build pasta-and-marshmallow based structures to understand basic concepts of engineering statics. Additionally, Rafael and Michael have co-taught their second Northwestern *Splash!* session where they explained the extraordinary mechanical performance of spider silks to middle- and high-school students.

**Data Management and Open Access**. Results of all experimental measurements and computational simulations are recorded in lab notebooks on a daily basis by individual researchers. In addition, each researcher is required to maintain a notebook that records and dates ideas that are discussed during research meetings. Together, these comprise the metadata collected by the project and take the form of descriptions and suitable citations of experimental apparatuses and procedures, descriptions and recipes of sample preparation and materials synthesis, description of computer codes, and computer calculation input conditions. All data types will be stored for a minimum of three years following the final date of the project or following the date of public release, whichever comes later. Metadata in the form of documentation of supplementary material, analysis files, and electronic journal entries are stored alongside data to make the data reusable. Additional related information including literature references, interim reports, research papers resulting from project, and the original bid proposal are stored on the groups’ local servers and will also be maintained for a minimum of three years after the ending of the project. All the data are publically accessible upon individual request.

**Publications**

1. M.R. Roenbeck, X. Wei, A.M. Beese, M. Naraghi, A. Furmanchuk, J.T. Paci, G.C. Schatz, and H.D. Espinosa, In situ scanning electron microscope peeling to quantify surface energy between multiwalled carbon nanotubes and graphene. ACS Nano 8, 124-138 (2014).
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5. C. Shao, S. Keten, Stiffness enhancement in nacre-inspired nanocomposites due to nanoconfinement, submitted to Adv. Mater.
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# Computationally Driven Discovery and Engineering of Multiblock Polymer Nanostructures using Genetic Algorithms.

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**Keywords:** Block Polymers, Self-Assembly, Inverse Design, Global Optimization

### Project Scope

We propose an approach for accelerating the design and discovery of novel self-assembling nanoscale block polymer microphases. For these systems, we tackle two computational problems that limit the rate of materials development: (i) the "forward problem" – given a polymer formulation, compute the most stable self-assembled nanostructure; and (ii) the "inverse problem" – given a target structure and properties, select the least complex polymer formulation that achieves the target. Our program is combined with the development of synthetic methods for new sequences of multiblock polymers and characterization methods for complex phases. In addition, we will develop a community-accessible web portal for computation and data mining.

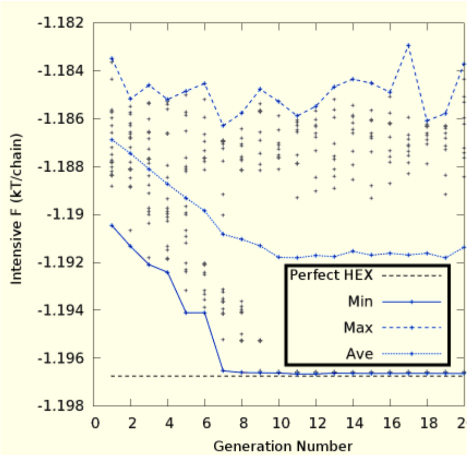

**Figure.** Evolutionary algorithm global optimization combined with self-consistent field theory local optimization successfully navigates the rough free-energy landscape, locating the globally stable structure in fewer than 10 generations, for the hexagonally packed cylinder phase of a melt of diblock copolymers (in this test case the target is known). This success is yet to be repeated for complex network phases.

### Relevance to MGI

We tightly integrate three components: (i) a new computational approach for identification of thermodynamically stable phases of a specified block polymer formulation; (ii) new synthetic strategies for fine control of composition and sequence of multi-species, multi-block polymers; and (iii) advanced characterization of novel phases. In an iterative approach, the synthesis and characterization assist with refining free interaction parameters in the theoretical model, and the computational search identifies interesting synthetic targets in the high-dimensional phase space.

### Technical Progress

The computational component of our project involves the use of molecularly informed statistical field theory formulated for melts of multi-species, multi-block polymers. We use the mean-field approximation to arrive at a self-consistent field theory (SCFT). SCFT is a quantitatively accurate method for computing the nanoscale self-assembly characteristics of high molecular weight block polymer melts. However, the free energy landscape for candidate structures is exceptionally rough, and consequently the computational discovery of new phases, without experimental guidance, is difficult. The problem is further compounded by the enormous design space of constituent polymers, which grows geometrically as the number of chemical species and number of polymer blocks increases. As an example, the class of tetrablock terpolymers has nine topologically distinct block sequences, and for each there are 13 free composition and interaction parameters that can be tuned to affect self assembly characteristics. Clearly, exhaustive mapping of phase diagrams for advanced multiblock polymers is of very limited utility.

We propose solutions for both the forward problem and the inverse design problem. The forward problem describes the difficulty of attaining the thermodynamically stable self-assembled structure from an unguided SCFT relaxation. For this task, we are developing a real-space genetic algorithm as a global optimization wrapper around the SCFT local optimization software. To validate the method, we have applied it to known phases in melts of diblock copolymers. The current method is successful for obtaining non-network phases such as hexagonally packed cylinders (see Figure), whereas network phases such as double gyroid are presently not found.

In parallel, we are developing an approach to tackle the inverse design problem. For a given target self assembled structure, we use particle swarm optimization methods to select the polymer constituents that assemble in the target structure. This approach is already proving to be useful for obtaining challenging motifs from directed self assembly of block polymers for application to lithographic patterning of microelectronic circuits.

## Future Plans

Once our genetic algorithm is sufficiently mature, we will begin applying it in a structure discovery mode for novel tetrablock terpolymer melts. The synthetic component of our program tackles the sophisticated methods required to finely control composition and block sequence for any of the nine sequences of tetrablocks consisting of poly isoprene (I), poly styrene (S), and poly ethylene oxide (O). We will initially target ISIO and SIOS, for which bulk morphologies are unexplored. Systematic variation of block molecular weights with low dispersity has already been achieved, and a library of such polymers with different compositions is being created. Characterization of phases with DSC, TEM and SAXS is in progress.

The combination of synthesis, characterization and computation will be employed iteratively to refine the interaction parameters present in the coarse-grained theoretical model underpinning SCFT, and to direct synthesis to parts of phase space with predictions of new or unusual phases.

## Broader impact

Our DMREF program engages four graduate students and one postdoc. Each already has well-developed expertise in their own activity areas, but are broadening their horizons in iterative interactions across disciplines. UMN-based scholars participate in the popular “Energy and U” outreach program. UCSB-based scholars are engaged in a variety of successful programs hosted by the Materials Research Laboratory (MRL), including Ask-a-Scientist, CISEI, and K-12 outreach. Our web portal will engage non-theorists in computational research.

## Data Management and Open Access

We are developing a web portal for registered users to perform structure discovery calculations in “forward mode”, utilizing the genetic algorithm global optimization method around our SCFT software. Historic calculations will be searchable for reducing redundancy. We also plan to make accessible our genetic algorithm wrapper software.

## Publications

1. D. Düchs, K. T. Delaney, and G. H. Fredrickson, *A multi-species exchange model for fully fluctuating polymer field theory simulations*, J. Chem. Phys. **141**, 174103 (2014).

# Integrated Mesoscale Architectures for Sustainable Catalysis

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**Keywords:** catalysis, multiscale modeling, surface reactions.

## Project Scope

The central theme of the IMASC project is to develop a detailed understanding of mechanisms and dynamics of catalyzed transformations, and to contribute to the design and controlled synthesis of catalytic structures, from a multiscale approach, ranging in scope from the atomistic to the macroscopic; these goals will be met by determining new paradigmatic models for controlling activity and selectivity of sustainable, complex reaction pathways for hydrogenation and oxidation reactions, which in turn will be achieved by relating the electronic and structural properties of catalyst materials and architectures. New multiscale computational methodologies will be developed, calibrated in model systems, and applied to predict and guide experimental searches over a wide range of possible reactant/substrate combinations that lead to desired products.

## Relevance to MGI

The scientific objectives of IMASC include (1) mastering the synthesis of novel porous metal alloy and metal oxide catalysts with specific active sites for activation of key reactants; (2) controlling selectivity of complex, coupled reactions for important pathway-dependent chemical processes; and (3) optimizing the design of meso-structured architectures for most efficient reactivity. In all three aspects, tightly knit teams of experimentalists and theorists will be working toward testing key hypotheses, derived from computational searches, and validating and further exploring the implications of the models by tailored experiments. More specifically, our design of catalytic materials will be based on the use of a minority active component to create key reactive intermediates that can migrate to the majority less reactive host in order to promote selective chemical transformations. We will investigate, both theoretically and experimentally, key hydrogenation and selective oxidation reactions that are important for large-scale chemical synthesis.

## Project Methods

By combining foundational experimental and theoretical approaches, IMASC will develop and interconnect basic understanding of catalytic phenomena using a multi-scale, multi-faceted approach. The complexity of materials to be studied will range from model flat and textured surfaces of single crystals to mesoporous materials. Reaction studies will link ultrahigh vacuum (UHV) to working catalytic conditions. These studies will span the range from detailed atomic-scale investigations on model flat and curved alloy surfaces (STM and TEM

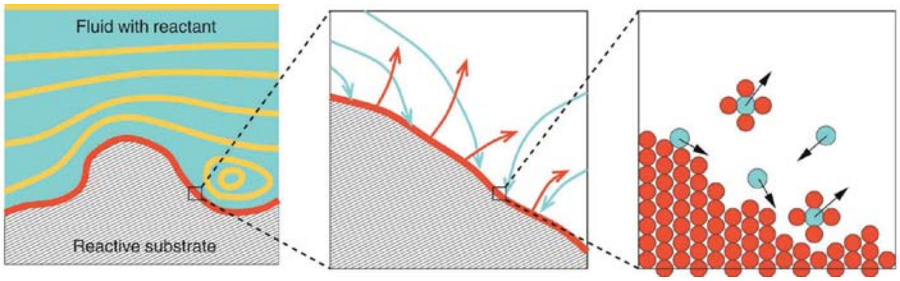

**Figure 1:** *Schematic representation of the scales involved in the reactivity of nanoporous catalysts, from the macroscopic (fluid flow regime) to the mesoscopic (transport of reactants and products to/from surfaces) to the microscopic (atomic-scale reactions).*

experiments) to X-ray studies that can identify the signatures of reactants and products in various configurations, to conditions that resemble industrial settings with model nanoporous reactors. The theoretical modeling will encompass all relevant scales, from the atomistic (treated with high-level accurate quantum mechanical methods based on Density Functional Theory) to the mesoscopic (treated with continuum theories based on Lattice Boltzmann equation); this is schematically shown in Fig. 1. Interconnections between scales will be explored, including the effect of surface curvature and surface coarsening during reactions at the mesoscale, to the atomic structure of surface features that promote reactivity.

## Future Plans

We have been able to reproduce the essential features of reactant and product flow through and around a nanoporous ingot, using a two-fluid reactive flow model in the context of the Lattice Boltzmann equation, as shown in Fig. 2. The challenge in these simulations was to capture the realistic flow patterns in the limit of high Knudsen number flow in the immediate neighborhood of the catalytic surface. These results closely match experimental findings in what concerns the distribution of reactants and products on the surfaces of the ingot, as well as the overall reaction yield. The results of these simulations will be used in two different ways: first, they will be employed in searches for optimal shape of the nanoporous structure that will give the highest product yield; second, they will be analyzed in terms of the molecular velocity distributions around surfaces of various orientations and curvatures, which provide the necessary boundary conditions for modeling the reactivity at the atomistic scale. We are also performing atomic-scale simulations of various prototypical surfaces, under static conditions, using quantum mechanical approaches. The results of the atomistic and meso-scale simulations will provide a comprehensive picture on the design of catalysts that can selectively promote the desired reactions.

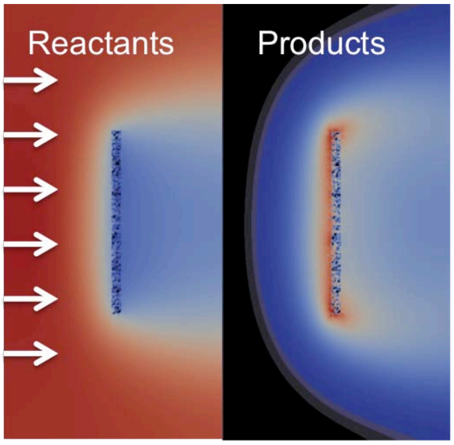

**Figure 2:** *Model of macroscopic flow through and around nanoporous ingot (at the center of the figure). For both reactants and products, red (blue) represents highest (lowest) concentration.*

## Broader impact

Through a rich, collaborative research effort, the IMASC project promises to provide fundamental understanding at the frontiers of discovery in sustainable catalysis. The exploration of wide range of possible surface structures and architectures from the microscopic to the mesoscopic scale, in a materials genome type of approach, will guide experimental realization of optimal design of heterogeneous catalysts. Understanding reaction kinetics, building new innovative architectures and improving reaction selectivity will (1) lead to new opportunities to decrease fuel consumption and (2) create more efficient and selective processes with benign byproducts. The students and postdocs involved in the project will gain the necessary skills and knowledge to become leaders in the field, having been exposed to state-of-the-art experimental and theoretical methodologies. Significant leeway is give to the junior researchers in the project to develop collaborations and take intitiative in specific projects, exposing them to leadership skills and goal-oriented research.

## Data Management and Open Access

The codes and methodologies developed through this project will be made publically available through a website that will contain a repository of all source materials and tutorials.

# Non-Adiabatic Molecular Dynamics Methods for Materials Discovery

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**Keywords:** Ab-initio Molecular Dynamics, Non-Adiabatic Couplings, Electronic Excitations, Time-Dependent Density Functional Theory, Surface Hopping

### Project Scope

The goal of this project is to provide robust, predictive, and broadly applicable computational tools enabling non-adiabatic molecular dynamics (NAMD) simulations in real materials with unprecedented accuracy and realism. We aim to develop a general-purpose code enabling 10-100 picosecond ensemble NAMD simulations for molecules and nano-sized clusters with ~100 atoms at the level of hybrid time-dependent density functional theory (TDDFT).

### Relevance to MGI

The rate of breakthrough discoveries in energy-related materials sciences depends crucially on our ability to control non-adiabatic transitions between electronic states. For example, sensitizer dyes for solar cells should exhibit large transition probabilities from the absorbing state to the charge-injecting state and minimal losses through other channels. NAMD simulations are the method of choice for these challenges. They provide direct access to observables such as quantum yields, time constants, and kinetic energy distributions which can be compared to accurate calculations and gas-phase experiments.

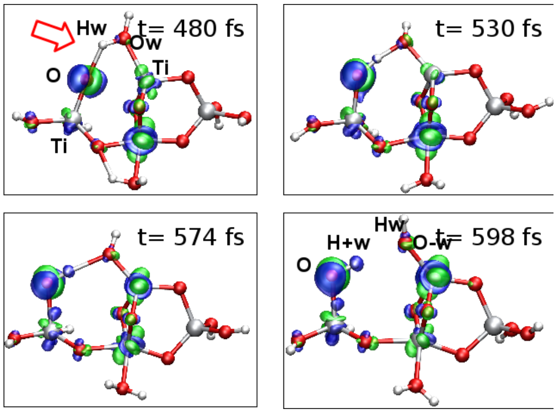

**Figure.** Sample B3LYP/SVP NAMD trajectory showing photoinduced water splitting in the $S_1$ state of $(TiO_2)_4$ clusters at 278 K. No reaction is observed in the ground state.

### Technical Progress

A highlight in FY 2014 was the development of improved iterative subspace algorithms for large-scale response calculations which lie at the heart of materials simulations. The simple but effective idea underlying this method is to exploit the reduction of the residual norms as convergence is reached. The method is particularly successful when Coulomb and exchange portions of the linear response equations are separated and in combination with fast factorization techniques such as the resolution-of-the-identity (RI) approximation. Up to five-fold speedups were observed in TDDFT calculations, with larger benefits for larger systems. This significantly extends the scope of NAMD simulations. Another important accomplishment was the extension of TDDFT-based NAMD simulations to open-shell systems enabling the simulation of homolytic bond breaking, which is very common in photochemical reactions. Previously, excited-state homolytic dissociation could only be addressed by multi-reference calculations, which are limited to molecules with few atoms. The present developments make it possible to obtain a qualitatively complete picture of photochemical reactivity for systems with up to 100 atoms for the first time. Further, we have completed the derivation and a first implementation of first-order non-adiabatic couplings between two excited states in the hybrid TDDFT framework. The result is consistent with time-dependent response theory, but also reveals an incorrect pole structure of the quadratic TDDFT response within the adiabatic (zero frequency) approximation for the exchange-correlation kernel. This result highlights the importance of frequency-dependent kernels for NAMD simulations. In the meantime, an approximate version of the couplings that becomes exact at conical intersections is the most promising candidate for applications. We have also developed a semi-numerical algorithm for efficient computation of non-local density functional exchange- and correlation energies. The integration over the relative coordinate is performed analytically using a new recursion to generate intermediate integrals that are functions of the electron center-of-mass. Integration over the center-of-mass coordinate is carried out numerically using standard molecular integration schemes. This makes it possible to use of local range-separated hybrids without empirical parameter tuning which is crucial for predictive modeling. First results show a surprisingly good performance for bond dissociation energies. In collaboration with the Heyduk group at UC Irvine, we have characterized the electronic structure of complexes of Group V metals with the redox-active tridentate (ONO) pincer ligand. While (ONO) complexes of Nb and Ta exhibit closed-shell ground states with completely oxidized $d^0$ metals, the V complex has a diradical ground state with an antiferromagnetic coupling between the $d^1$ metal atom and the semiquinoidal (ONO) ligand, which explains the intense MLCT band of the V complex in the visible spectrum and demonstrates the promise of the (ONO) ligand platform for charge-transfer dyes. We have performed NAMD simulations on photoexcited titania nanoclusters in collaboration with Enrico Berardo and Martijn Zwijnenburg (UCL) to invesigate the promise of this material in photocatalytic water splitting. First results indicate that photoinduced water splitting can occur in the first excited state of $TiO_2$ tetramers, see Figure.

## Future Plans

In the remaining year, we will complete the shared-memory parallelization of our NAMD code and explore further acceleration by graphics processing units. We will also develop an algorithm to efficiently compute couplings between many states. We will test decoherence corrections and investigate local diabatization methods. We will continue to perform demonstrative applications.

## Broader impact (Optional for DOE grants/FWPs)

During the past two years, two high school students, three undergraduate students, two graduate students, and two postdoctoral researchers were trained in ab-initio NAMD simulations and their application to molecular materials. Partly as a result of their participation, one high school student accepted an offer to study chemical engineering at Columbia University, two undergraduate students received departmental awards, and one postdoctoral researcher obtained a faculty position at Cal State Long Beach. The material developed in this project is being used for undergraduate and graduate classroom education in theoretical and computational chemistry at UC Irvine. We have developed a 3-minute video introduction to ab-initio NAMD simulations that is publically available on YouTube. The PI has given pedagogical lectures at predominantly undergraduate institutions and high school teacher workshops to educate the broader public on computational materials research.

## Data Management and Open Access

The software developed in this project is publically available through the Turbomole program package. The source code is archived in the Turbomole SVN repository after it satisfies Turbomole's coding standards and passes the Turbomole test suite. Once the code has been checked in, it can be accessed by all Turbomole developers. Any outside individual or organization can request Turbomole developer status and obtain access to the entire Turbomole source code by submitting a code development proposal to Turbomole. In addition to the distribution through Turbomole, newly developed code can be shared upon request for research and teaching purposes. While Turbomole is proprietary software, the code developed in this project is co-owned by its developers, and no restrictions are imposed on its use in education and research. Turbomole has adopted an irrevocable non-profit clause in its articles of incorporation, and its balance sheets are published on the web. The license fees are mostly used to provide high quality user support, to develop tools such as a graphical user interface to enhance accessibility, and to maintain long-term code stability. Discounted licenses are available for teaching, undergraduate institutions, and students.

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4. S. Hanaouchi, B. T. Krull, J. W. Ziller, F. Furche, and A. F. Heyduk, *Metal effects on ligand non-innocence in Group 5 complexes of the redox-active [ONO] pincer ligand*, Dalton Trans. **43**, 17991 (2014).

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# Inorganometallic Catalyst Design Center
# Energy Frontier Research Center

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**Keywords:** Catalysis • Metal clusters • Electronic structure methods • Metal organic frameworks • Hydrocarbon activation • Synthesis

### Project Scope

The Inorganometallic Catalyst Design Center (ICDC) will computationally guide the discovery of a new class of energy-science-relevant catalytic materials and understand the underlying structure-function relationships that will lead to further catalyst discovery. The mission of the ICDC encompasses developing supported cluster catalysts with the following characteristics:

- Uniform mesoscale structures that can be synthesized reproducibly, ideal for both **experimental characterization** and **computational modeling**.
- Clusters that are **well-defined and uniform in structure and composition**, but isolated from each other.
- Catalyst structures amenable **to high-throughput experimental screening**, very reliable **quantum mechanical predictions** on prototype exemplars, and **computational high-throughput screening**.

### Relevance to MGI

One core of the ICDC revolves around advanced modeling for *in silico* design of new catalysts of potentially extraordinary activity and selectivity; the other core revolves around the experimental realization of these species. The design approach will be accelerated by structural, energetic, and mechanistic modeling coupled with selective, high-throughput computation. The ability to test hypotheses *in silico* over an enormous and arbitrarily modifiable database of hypothetical catalysts is expected to lead to compelling, transferrable catalyst design rules and potentially lead to the discovery or design of new mechanisms and desirable new catalytic chemistry.

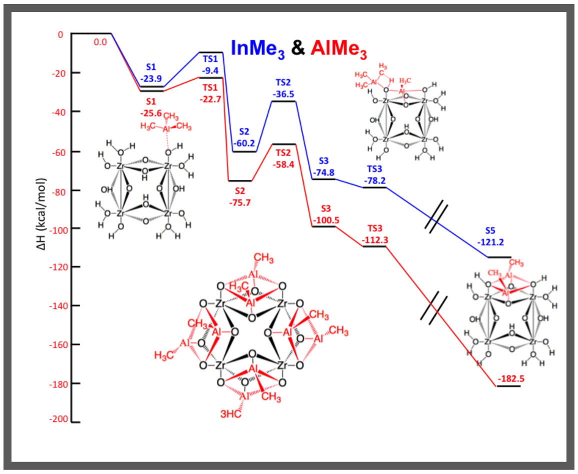
### Technical Progress

ICDC started in August of 2014. In the following five of the ongoing efforts are described.

1) We performed computer simulations to predict the mechanism and ultimate structure of metal clusters deposited on NU1000 nodes. A detailed understanding of atomic layer deposition (ALD) of metal clusters at the $Zr_6$ nodes and of possible catalytic activity will allow us to design novel catalysts. Our major achievements are: a) Theoretical modeling has established the step-by-step details and overall thermochemical driving force for

deposition of different ALD precursors. b) Theoretical structures have assisted in the refinement of X-ray powder diffraction data. c) In-situ IR has played a key role in identifying intermediate structures and the role of node dehydration under operating conditions.

2) To address the persistent long-term scientific need for higher accuracy theories at lower computational cost we have developed a theory, called multiconfiguration pair-density functional theory (MC-PDFT), which combines wave function methods with density functional theory. The method is much less expensive than other post-Hartree-Fock methods for calculating the dynamical correlation energy starting with a multiconfiguration self-consistent-field wave function as the reference wave function. Initial tests of the theory are quite encouraging. We have tested the theory by applying it to bond energies of main-group molecules and transition metal complexes, barrier heights, and reaction energies for diverse chemical reactions, proton affinities, and the water dimerization energy.



**Atomic layer deposition of Group III metals:** The NU-1000 core has four distinct faces, two exposed to large pores and two exposed to small pores. InMe3 and AlMe3 react with exposed OH groups to deposit eight metal atoms in a structure predicted by theory and confirmed by X-ray powder diffraction.

3) We are using preassembled metal-metal complexes to enable the introduction of diverse combinations of earth abundant metals onto a solid support. With a library of heterobimetallic complexes in hand, we screen these complexes as potential precursors for installing mixed-metal sites onto zirconia nodes of NU-1000. Theory is employed to validate experiment and to predict yet unsynthesized structures.

4) We are investigating the bonding sites of $Zr_6$ nodes in NU-1000 and UiO-66 for single-iridium-atom complexes by preparing various loadings of iridium complexes ($Ir(C_2H_4)_2$ or $Ir(CO)_2$), that is, synthesizing and characterizing samples with iridium loadings of 1, 5, 10, and 20 wt. We use IR spectroscopy to characterize the carbonyl ligands in $Ir(CO)_2$ and investigate the reactivity of this complex with $C_2H_4$. Calculations are underway that provide insight into the bonding of the iridium complexes to the $Zr_6$ nodes and also investigate the reaction pathways in ethylene hydrogenation and dimerization catalyzed by the node-supported iridium complexes.

5) An isoreticular series of metal-organic frameworks (MOFs) with the topology based on zirconium oxoclusters and tetracarboxylate linkers with a planar core (NU-1101 through NU-1104) has been synthesized employing a linker expansion approach. In this series, NU-1103 has a pore volume and a geometric surface area, which are the highest value reported to date for a zirconium-based MOF, and among the largest that have been reported for any porous material. The agreement between measured and simulated values for pore volumes and surface areas suggests the successful activation of the MOFs, with NU-1103. Additionally, NU-1103 retains its structural integrity after soaking in water.

## Future Plans

The ICDC team is working in a synergistic computational and experimental effort, in which the ultimate goal is to achieve an energy-efficient liquefaction of natural gas, either by catalytic conversion to alcohols or by catalytic conversion of C1, C2, and C3 species to C6 to C10 hydrocarbons.

## Data Management and Open Access

In collaboration with the Argonne National Laboratory, ICDC will develop a database of computationally predicted catalysts and their properties. This accessible technical tool will aid the discovery of novel catalysts and also serve as repository for computational and experimental data generated by ICDC.

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# Nitride Discovery
# Creating the Knowledge Base for Hard Coating Design

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**Keywords:** hard coatings, mechanical properties, density functional calculations, transition metal nitrides, epitaxy.

## Project Scope

This research program develops a systematic method to determine the intrinsic physical properties of transition metal nitrides. A combination of measurements on epitaxial single crystal layers and density functional calculations are used to create a complete data set of the elastic properties and hardness for all 30 nitrides. This data set is the basis for an interactive ceramics property database tool which is developed as an integral effort of this research program and is envisioned to dramatically accelerate discovery of hard, wear resistant coatings and transform the evolutionary trial-and-error development of protective coatings into a coatings-by-design approach.

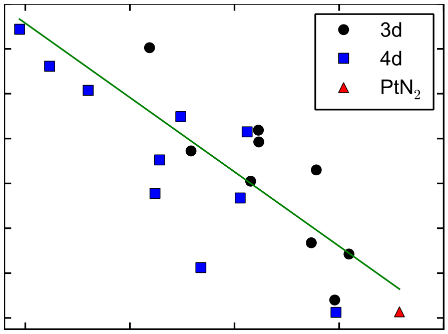

**Figure:** Density of States (DOS) at Fermi energy versus shear modulus $C_{44}$ for stable per-nitrides $MN_2$. Transition metals M are from 3d or 4d rows. $PtN_2$ being super-hard is shown distinctly.

## Relevance to MGI

Continuous close cross-fertilization between first-principles predicted properties, nano-indentation measurements, and thin film processing is essential to develop the complete property dataset. In particular, (i) simulations determine the elastic anisotropy which is essential to correctly interpret the measured indentation moduli, (ii) the measured hardness confirms or corrects empirical hardness-vs-elastic-constants correlations that are used to predict hardness from first-principles, (iii) thin film deposition and subsequent experimental characterization defines the compositional and structural space that needs to be simulated, (iv) computations provide systematic data for all nitrides, including those for which accurate intrinsic property measurements are unattainable due to still missing synthesis routes.

## Technical Progress

The technical achievements and related publications can be grouped in three areas:
*(1) Overview studies* [4,7-9] which systematically compare structural, energetic, elastic and mechanical properties with the electronic structure of transition metal nitrides. More than 200 structures with metal (M) to nitrogen ratios ranging from 0.5 to 4 are studied, including $M_4N$, anti-$ReO_3$ ($M_3N$), niobium oxide ($M_3N_3$), rocksalt ($M_4N_4$), cesium chloride ($M_4N_4$), zincblende ($M_4N_4$), fluorite ($MN_2$), and pyrite ($MN_2$). One key finding is illustrated in the Figure: The shear modulus is anti-correlated to the density of states at the Fermi energy. This provides, due to the strong correlation of the hardness with $C_{44}$, a direct path for prediction of super-hard nitrides. For example, $PtN_2$ has a negligible DOS, a high $C_{44}$ = 129 GPa and a resulting very high hardness of 23.5 GPa. For this pyrite structure, a panoptic view involving a complex interplay between iconicity, metallicity and covalency is shown to explain hardness in these compounds. Such an analysis may function as a broad framework for the understanding of hardness in other systems as well.

*(2) Detailed studies* [1,2,6,13] on specific promising nitrides where materials synthesis, characterization, and property predictions are combined to gain a new understanding of correlations between composition, structure, and mechanical properties. In particular, epitaxial layers of $WN_x$, $NbN_x$, $NbC_xN_{1-x}$ are deposited by reactive sputtering, their composition and strain state analyzed and their elastic and mechanical properties measured by nanoindentation and Brillouin scattering. Direct correlation of the measured composition dependence of lattice and elastic constants with first-principles predictions yields new insights, including a ductile-to-brittle transition with increasing $x$ in $NbC_xN_{1-x}$, a strong anisotropy in elastic constants that causes a strong texture dependence in the hardness of $WN_x$ coatings, and an unexpected composition dependence in the $NbN_x$ lattice constant that is kinetically limited and controls its mechanical properties.

*(3) Exploratory studies* [3,5,10-12,14-20] that emerge from the developed synergistic theory-experiment collaboration, go beyond the core goals of the project, and catalyze new transformative research efforts. Examples include a study on ScN, where measurements of optical and electronic transport in epitaxial layers is combined with predictions of the dielectric function by hybrid exchange correlation density functional calculations, providing the band gap value of this novel semiconductor, or a study on the electron mean free path in TiN(001) which involves *in situ* electron transport measurements on 2-nm-thick layers and first-principles prediction of the ballistic transport.

## Future Plans

(i) The next step towards elucidating the nature of hardness is to study the effects of interfaces, deviations from stoichiometry, and alloying. (ii) The public database will be populated further by our own computational and experimental data as well as from the scientific literature.

## Broader impact

This project has directly impacted a total of 7 graduate and 6 undergraduate students that have been working collaboratively to determine the intrinsic mechanical properties of transition metal nitrides. They have been trained in materials synthesis, characterization, and computational methods relevant to the hard coating industry. In addition, they have developed a community-driven ceramics database to educate the interested general public about nitride properties and to provide accessible data that is essential to academic and industrial development engineers who design new hard coatings. Open access software has been generated to speed repetitive complex computations of structural, elastic and mechanical properties of single crystal materials, which will impact research in a wide range of ceramics.

## Data Management and Open Access

We have created a centralized platform for storage, search and analysis of single crystal data related to structure, composition, elastic and mechanical properties for ceramic materials. Electronic, optical, thermal, tribological and other properties may be added to the database on demand. The database is free, open access, user-friendly and community driven. Data stored in the database is expected to be populated by contributions from the world-wide research community. Responsibility for ownership of results, their veracity and accuracy will be the responsibility of the contributors. For this purpose, a direct online DOI original source citation feature is available. A user may engage with the database as a data contributor with full control of the entered data in terms of addition, correction or deletion. Another way to benefit is to access data contributed by others. In this latter mode, user-specified tabular display and graphical display of trends in searched results is facilitated. Downloading of a sub-set of the searched data is available. Finally, external links to origins of the data in cited papers and contact information about the contributor or paper authors is accessible. The backend data structure has been designed for increase of size and features as demand increases.

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# Multiscale Theory and Experiment in Search for and Synthesis of Novel Nanostructured Phases in BCN Systems

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**Keywords:** BCN system, phase transformations, high pressure, shear, multi-scale simulation, rotational diamond anvil cell.

### Project Scope

Our *goal* is to advance multiscale theory, modeling, and experiment to enable a revolutionary new approach to search for and synthesize nanostructured superhard phases in BCN systems under *high pressure and shear*. We combine theory, simulations, and experiment to achieve to search for new nanostructured superhard phases, to dramatically reduce the pressure required for phase transformations, and to stabilize these high pressure phases for processing at ambient pressure utilizing a unique rotational diamond anvil cell (RDAC) for large *plastic shear deformation* at high pressure. We focus on: superhard phases of carbon, boron, cubic and wurtzitic boron nitride, cubic $cBC_2N$, $BC_4$, high density $C_3N_4$, and other phases and nanostructured composites.

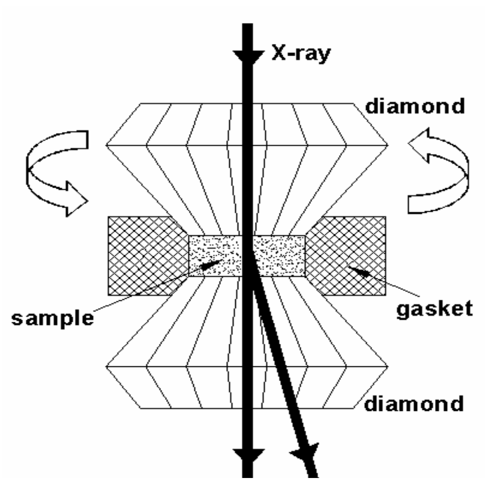

**Figure 1.** A rotational diamond anvil cell. By rotating one diamond anvil under axial loading, this apparatus generates large plastic shear under high pressures in studied materials. It permits in situ X-ray and spectroscopic characterization of materials during phase transformation.

### Relevance to MGI

We will use *first-principles* based theory and atomistic *reactive dynamics* simulations to predict the transformation, stability, and properties of material polymorphs, phases, and intermediates over a wide range of pressure and shear. These simulations will be supplemented with *continuum level* simulations at nano-, micro-, and macro-scales. Our RDAC with in situ synchrotron X-ray measurements is utilized to experimentally realize the processing optimal pressure-shear loading path predicted from the simulations to make proposed materials.

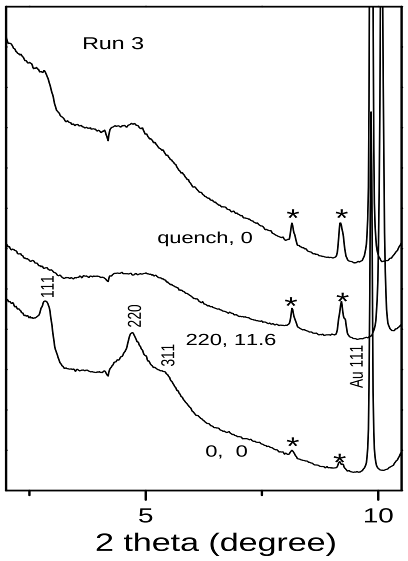

**Figure 2.** XRD patterns of sheared $C_{60}$ at pressures. Rotation Angles of in degree and pressure in GPa are given below the patterns.

### Technical Progress

- ***Atomistic modeling***--Our initial design of BCN systems with improved mechanical properties, used density functional theory to examine modified BCN structures based on the boron carbide structure ($(B_{11}C_p)CBC$. We found that substitution of one cage carbon atom with nitrogen, to form $(B_{11}N)C2$ leads to improved hardness. However, our studies of shear deformation along the most plausible slips system, (01-1-1)/<-1101>, suggests that the new structure will not improve ductility. Thus, we are now examining a new structure of $(B_{12})(NH)_2$ we propose will have better hardness and lower density. We are examining shear deformations to examine the ductility properties.

- ***Continuum modeling--***Phase field model for coupled phase transformation and dislocation evolution is developed and first finite element study of their mutual effect is performed.
- ***Amorphousation of $C_{60}$*** --We applied shear under pressure on $C_{60}$. $C_{60}$ is found to transform into amorphous phases at above 5.7 GPa, one of which is quenchable to ambient conditions. Further characterization is underway. See Figure 2.

**Future Plans**

- To use first-principles based theory and atomistic reactive dynamics simulations to predict the transformation, stability, and properties of material polymorphs, phases, and intermediates over a wide range of pressure and shear in an extensive series of *in silico* studies and to find the optimum combination of shear and pressure for various materials within BCN system.
- To advance three-scale continuum theory for plastic strain-induced phase transformations under high pressure and utilize it to model synthesis of nanostructured superhard phases in RDAC, to find ways to control (i.e., promote direct and suppress reverse PTs) PTs and to seek for new phases.
- To perform strain-induced synthesis experiments in RDAC with in situ diagnostics to realize the optimal pressure-shear loading path predicted from the multiscale simulations.
- To iteratively couple modeling at each scale and experiments to improve models and identify material parameters, to optimize experimental search for new loading paths, phases, and nanostructures, as well as the ways to reduce transformation pressure and keep high pressure phases at ambient pressure.
- To seek for, study and utilize new strain-induced phenomena, phases, loading programs, and unprecedented material properties.

**Broader impact**

Superhard materials have numerous applications in cutting, polishing, and drilling tools for various industries (including the oil industry) and as components of composite materials. Progress in synthesizing new superhard materials stable at ambient conditions may revolutionize these fields. The approaches developed in this project may be expanded to achieve unique properties for other material systems . One graduate student, 2 post docs, and 2 undergraduate students will receive training on Multiparadigm simulations and experiments. Special programs at Caltech, ISU, and TTU are being used to attract students from under-represented groups. Two new graduate courses on strain-induced PTs and high pressure physics and experimentation will be developed by the PIs. Results obtained here will be disseminated broadly via seminars, workshops, conferences, and short courses. Special symposia devoted to the interaction of PT and plasticity will be organized at various international conferences.

**Data Management and Open Access**

The data will be published in public journals and proceedings. After publication, the copyright is granted to the publisher. After publication, the data can be accessed by the public for non-commercial purposes. The data can also be shared in collaborations with the data creators. The data user can access the information through published journal without of charge for data access. The use of the published data is also granted under conditions of proper acknowledgement and references. For reproduction, the individual publisher's guidelines must be followed. The long term maintenance and preservation of the database also rests with the journal, which has the safeguards and the longest-term-storage capability.

The metadata will be stored and displayed through the Texas Tech University website. The metadata will include the experimental data, the data analysis, and the conclusive points along with the references to the journal where the data is published. The metadata will be updated within 3 months of obtaining new data . We will store the data for 3 years.

# Design of Multifunctional Catalytic Interfaces from First Principles

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**Keywords:** Heterogeneous catalysis, Density Functional Theory, Metal-oxide interfaces, Water-gas shift reaction

### Project Scope

This project seeks to develop design rules and multifunctional catalysts for reactions occurring at metal/oxide interfaces. We will combine periodic Density Functional Theory (DFT) calculations, advanced synthesis techniques, rigorous measurements of reaction kinetics, and high resolution TEM characterization to understand the atomic-level structures of metal/oxide interfaces and to predict trends in the reactivity of these interfaces for model reactions such as water-gas shift. The identification of robust correlations between activation barriers, binding energies, and structural/electronic features of the catalysts, as have been previously described for metallic catalysts, will permit the development of quantitative reactivity predictions and, ultimately, genome-based catalyst screening.

### Relevance to MGI

This effort will develop a comprehensive, first principles-based modeling paradigm for multifunctional catalytic interfaces, including both supported catalytic metal nanoparticles and thin film oxides on metallic substrates. These materials have the potential to overcome fundamental bottlenecks associated with simpler catalytic structures. We will systematically develop detailed computational models of these interfaces, which will in turn be generalized to identify fundamental descriptors suitable for rapid computational screening of catalytic materials. These efforts will be tightly coupled with unparalleled atomic-scale experimental characterization, synthesis, and reactivity measurements to both inform the computational models and test predicted catalysts to emerge from the computational analysis.

### Technical Progress

We have initiated theoretical and experimental studies of water-gas shift (WGS), a model reaction that we believe will be significantly promoted at multifunctional catalytic interfaces. The work to date includes preliminary development of a computational database of relevant descriptors for WGS chemistry on bimetallic alloys, the generation of an experimental database of WGS kinetics on many metal/oxide support combinations to both guide and validate the computational efforts, and the elucidation of preliminary structural models of metal nanoparticle/oxide support interfaces.

### Future Plans

Although bifunctionality has long been studied for particular reactions and catalysts, the fundamental lack of atomic-level characterization of these systems has rendered systematic exploitation of interfacial/bifunctional phenomena difficult. The complexity of such systems, in turn, has prevented theoretical methods from making significant contributions. We are working to overcome these limitations using a combination of state-of-the-art computational modeling, experimental synthesis, characterization, and kinetic measurements at the molecular level. In particular, we will use first principles Density Functional Theory calculations, ab-initio thermodynamic analyses, genetic algorithm-based structural searches, and classical Wulff Theorum analyses of particles, together with advanced synthesis, environmental HRTEM, UHV-based STM, and kinetic characterization techniques, to develop efficient methods to predict catalyst structures given an initial catalyst composition and approximate reaction conditions. We will focus on two broad classes of metal/oxide interfaces: metal nanoparticles supported on well-defined oxide substrates, and thin (1-2 ML) oxide films supported on transition metal substrates. Our initial work will focus on the water-gas shift reaction. This reaction is both a classic model reaction in heterogeneous catalysis and relevant to a variety of practical chemistries, ranging from biomass conversion to hydrogen production from petrochemicals. The intermediates and elementary steps associated with WGS are also very relevant to, and serve as a basis for understanding, additional classes of reactions that we will later tackle, including synthesis from mixtures of CO, $CO_2$, $H_2$, and other feedstocks. We believe that these reactions are likely to be highly susceptible to improvements resulting from bifunctional effects. Predicted rates will be verified by close comparison with experimental studies on model supported nanoparticles and inverse catalysts, which our team can perform with extremely high accuracy. The models will be used to identify reactivity descriptors that will serve as a basis for subsequent computational catalyst searches.

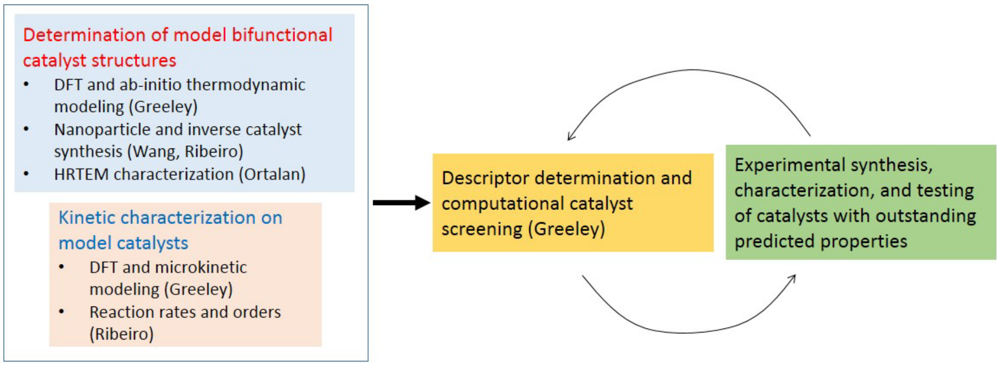

**Figure 3**. Project flow for design of multifunctional catalyst understanding and design, including PI contributions.

## Broader impact

The project will result in design principles for water-gas shift catalysts and will, in a more general sense, lead to a systematization of computational and experimental methods to identify improved multifunctional catalysts for a variety of industrially-relevant reaction chemistries. In the course of the project, multiple graduate students will be trained in state-of-the-art computational, theoretical, characterization (TEM), and kinetic techniques, and these students will take the obtained knowledge to future careers in academia and industry. Throughout the projects, the PIs will additional seek to make sustained and significant investments in the scientific and intellectual development of a targeted number of disadvantaged high school students at a very early stage in their academic careers, with a view to significantly increasing the probability of their choosing to attend a university (and to pursue STEM studies while there). The PIs will recruit multiple economically disadvantaged or underrepresented high school summer interns per year to their research groups. This effort will pair the students directly with the PIs and their graduate students and will have a distinct project for each intern. This direct secondary school research experience will be augmented by participation in seminars on catalysis research, to be held at Purdue University.

## Data Management and Open Access

This project will generate both electronic and print data which integrate experimental studies and molecular simulations. The print data will largely consist of procedures, notes, and observations recorded in laboratory notebooks, as is quite normal in the course of experimental research. The electronic data will include simulation codes and results, as well as data generated from analytical and spectroscopic instruments, and will be included in growing online databases. Publication in the peer-reviewed literature provides the primary means of disseminating and archiving the primary products of the research, including all laboratory and computational procedures, results, and analyses of those results.

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2. Z. Zhao, J. Greeley, *Identification of surface intermediates during ethylidyne formation on Pt(111) by calculation of infrared intensities and deuterium isotope shifts,* submitted.

# High-Performance First-Principles Molecular Dynamics for Predictive Theory and Modeling

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**Keywords:** first-principles, ab initio, electronic structure, molecular dynamics, density functional theory.

## Project Scope

This project aims to develop scalable, high-performance software for First-Principles Molecular Dynamics (FPMD) simulations, and use it in investigations of materials relevant to energy conversion processes. FPMD simulations combine a quantum-mechanical description of electronic structure with the statistical description provided by molecular dynamics (MD) simulations. New algorithms are developed for i) efficient computations of electronic structure using hybrid density functionals, ii) computation of spectroscopic properties (Raman and infrared spectra), and iii) improved statistical sampling methods. The software is used in investigations of aqueous solutions and liquid/solid interfaces relevant to photo-electrochemical cells. The algorithms are implemented in the Qbox code, distributed under a GPL open-source license.

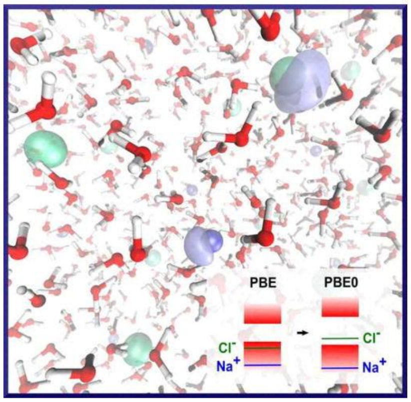

**Figure 1** Isosurfaces of orbitals in an aqueous NaCl solution computed using the PBE0 hybrid density functional. A correct localization of the HOMO orbital associated with the Cl anion requires the use of a hybrid density functional.

## Relevance to MGI

First-principles simulations allow for investigations of the electronic properties of materials in realistic conditions (e.g. finite temperature, or presence of defects). The approximations used in the simulations (i.e. the level of description of exchange and correlation in electronic structure) are validated by comparing predicted structural properties (e.g. pair correlation functions in liquids) and electronic properties (e.g. optical absorption, band gap, Raman and IR spectra) with results obtained in well-controlled experiments. Validated approximations are then used in predictive simulations of complex structures, such as solid/liquid interfaces.

## Technical Progress

***Algorithm development and implementation in the Qbox code:*** We have redesigned the most numerically intensive parts of the Qbox code to improve scalability on the BlueGene/Q architecture, enabling FPMD simulations of a 4096-atom silicon carbide (SiC) sample (16384 electrons) on 32k cores of ANL Mira (BlueGene/Q) in 22.8 s/SCF iteration. This enables MD simulations of similar systems for durations of several picoseconds. We have demonstrated electronic structure calculations of a 12288-atom SiC sample (49152 electrons) on 524288 cores of ANL Mira in 127 s/SCF step. This allows for DFT structure optimization for systems including over 10000 atoms. We have developed scalable algorithms for efficient electronic structure computations using *hybrid density functionals*, which are more accurate than conventional GGA-DFT functionals. We introduced a new load-balancing algorithm for hybrid DFT calculations combining a random search for an optimal distribution of orbitals among processors, and a replication of orbitals among processors[5]. These improvements enabled PBE0 calculations of the electronic ground state of a 4096-atom SiC sample (16384 electrons) on ANL Mira (BlueGene/Q) using 32k cores, with 6400s / SCF iteration.

***Ab initio simulations of the vibrational spectra of liquid water and of a solid/liquid interface:*** We have implemented an on-the-fly calculation of electric polarization and electric polarizability in Qbox, enabling simulations of infrared and Raman spectra, respectively. We have carried out the first ab initio simulations of the Raman spectra of liquid water by combining FPMD and density functional perturbation theory (DFPT). The computed Raman spectra are in good agreement with experiments. Our results highlight the importance of electronic effects in the interpretation of Raman spectra of liquid water[4]. We simulated the infrared spectra of water at the alumina (0001)/water interface, a prototypical oxide/water interface. The computed structural properties of the interface are in good agreement with synchrotron X-ray data. Analysis of the computed infrared spectra at the interface provides a molecular interpretation of the “ice-like” and “liquid-like” bands observed in sum-frequency vibrational spectroscopy experiments[2].

***Ab initio simulations of electronic excitations in water and aqueous solutions:*** We have carried out the first ab initio calculation of the absolute position of the band edges of liquid water using the GW approximation. We found that the level of theory chosen to generate molecular dynamics trajectories may substantially affect the electronic structure of the liquid. Our results represent an essential step toward the prediction of the relative position of water redox potentials and the band edges of semiconductors and insulators[3]. We have carried out ab initio PBE0 MD simulations of a dilute solution (1 M) of NaCl in water, and found that the perturbation of the water structure by the ions is mostly localized to their first solvation shell, in agreement with recent experiments. The PBE0 hybrid DFT predicts qualitatively correct positions of the energy levels of the ions with respect to the valence band of water[1].

***Development of advanced sampling algorithms for FPMD simulations:*** We have explored recently-proposed rare-event sampling methods that accelerate sampling of atomic configurations in systems having a complex energy landscape. We implemented these methods using a client-server model in Qbox, which allows for the coupling of a DFT calculation with a driver program that implements an arbitrary sampling algorithm. Using this approach, we have carried out an extensive series of simulations on liquid water with replica-exchange molecular dynamics (REMD) between the temperatures of 200 to 600 K and have made direct comparisons of the sampling efficiency to traditional first principles molecular dynamics simulations.

## Future Plans

Future research will focus on the development of scalable algorithms for the computation of the polarizability tensor using hybrid DFT, and applications to the study of sum-frequency generation spectra. We will further improve the scalability of hybrid DFT simulations beyond 128k cores. We will simulate Raman and IR spectra of oxide/water interfaces relevant to photo-electrochemical cells and energy conversion devices. We will adapt the design of the Qbox code to exploit new computer architectures, such as the projected Cori platform (NERSC).

## Data Management and Open Access

All software developed in this project is available under the GPL license. The Qbox code is available at http://eslab.ucdavis.edu/software/qbox. Pseudopotentials used in simulations are available at http://fpmd.ucdavis.edu/potentials/index.htm . Reference data (atomic trajectories) will be made available at http://www.quantum-simulation.org. A dataset of FPMD trajectories for liquid water is available online and is currently being analyzed. Statistical data (pair correlation functions, vibrational spectra) will be provided together with atomic trajectories.

## Publications

1. A.P.Gaiduk, C.Zhang, F,Gygi and G.Galli, *“Structural and electronic properties of aqueous NaCl solutions from ab initio molecular dynamics simulations with hybrid density functionals*”, Chem. Phys. Lett. **604**, 89 (2014).
2. P.Huang, T.A.Pham, G.Galli and E.Schwegler, “*Alumina(0001)/Water Interface: Structural Properties and Infrared Spectra from First-Principles Molecular Dynamics Simulations*”, J.Phys.Chem. C **118**, 8944 (2014).
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7. C. Zhang, T. A. Pham, F. Gygi, G. Galli, *"Electronic Structure of the Solvated Chloride Anion from First Principles Molecular Dynamics*, J. Chem. Phys. **138**, 181102 (2013) http://dx.doi.org/10.1063/1.4804621
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9. S. Wippermann, M. Vörös, A. Gali, F. Gygi, G. Zimanyi and G. Galli, *"Solar nanocomposites with complementary charge extraction pathways for electrons and holes: Si embedded in ZnS"*, Phys. Rev. Lett. **112**, 068103 (2014).

# Combinatorial Methods to Enable Rapid Prototyping of Polymeric Pervaporation Membranes for Biofuels

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**Keywords:** biofuels, combinatorial screening, polymer membranes, molecular dynamics, pervaporation

## Project Scope

A key challenge in the production of bioethanol and biobutanol fuels is their energy-efficient recovery from dilute aqueous fermentations. Pervaporation is a leading candidate to replace energy-intensive distillation processes. Through a synergistic program of high-throughput combinatorial experiments, data-driven thermodynamic modeling, and predictive molecular simulations, we are developing a rapid prototyping paradigm to accelerate design of *polymeric pervaporation membranes*. Our suite of complementary tools encompasses high-throughput synthesis and measurements, molecular dynamics simulations, and thermodynamic modeling of multi-component polymer-solvent systems.

## Relevance to MGI

Combinatorial synthesis of copolymer membranes produces a library of materials differing in two independent variables (e.g., hydrophilicity and crosslink density). Equilibrium swelling measurements in pure and mixed solvents provide thermodynamic interaction parameters for a multi-component, equilibrium thermodynamic model. Experimental data and interaction parameters are inputs to simulations, which predict component diffusivities in membranes. Computation of permeability selectivity and component transport rates completes the design loop by linking performance metrics with molecular structure.

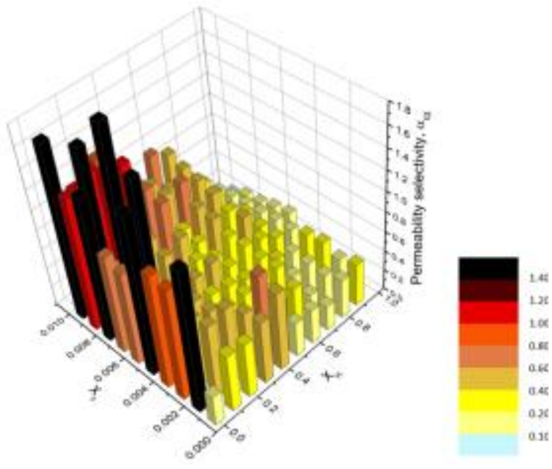

**Figure 1.** Permeability selectivity for a matrix of membrane materials having orthogonal gradients in hydrophilic unit mole fraction ($X_H$) and crosslinker mole fraction ($X_C$). This key deliverable relies upon high-throughput synthesis and swelling experiments, thermodynamic interaction parameters from a theoretical framework, and information about diffusivities from simulations.

## Technical Progress

A combinatorial method has been developed for rapid screening of copolymeric pervaporation membrane materials intended for alcohol-water separations. Polyacrylate networks based upon crosslinked random copolymers (hydrophilic + hydrophobic monomers) are a model membrane system for ethanol-water separation. Equilibrium selectivities and distribution coefficients for water and ethanol are obtained experimentally by combining equilibrium swelling measurements and high-throughput HPLC analysis. Simulation of the diffusivities of water and ethanol in each membrane provides the permeability selectivities (Fig. 1).

A four-component (two polymer, two solvent) extension of the classical Flory-Rehner theory with six independent binary interaction parameters ($\chi_{ij}$) has been developed. The combinatorial matrix of membrane materials is used to extract information about the $\chi_{ij}$, which are potentially concentration-dependent. Knowledge of the $\chi_{ij}$ yields an analytical expression for thermodynamic equilibrium at the membrane-liquid interface, which is an essential boundary condition for modeling of water and alcohol transport through a membrane.

Molecular dynamics simulation was employed to build structures via the simulated annealing polymerization technique to create polymers (without cross-linking), and the structures were relaxed through a stepwise cooling process to reach room temperature. Local translational motion of the solvent molecules (water and ethanol) was quantified using the mean-squared-displacement (MSD) of the center of mass of the molecules (**Fig. 2**). The motion of the water molecules is not diffusive, and the displacement of the water molecules was larger than the MSD of the ethanol molecules, while showing a strong concentration-dependent behavior. Membrane separation efficiency is governed by both the internal structure of the membrane and the relative concentration of water molecules. The effects of water concentration on the alcohol-water system are being investigated by characterizing local arrangements near polymer functional groups and the hydrogen bonding interactions in these systems. In addition, the composition dependence of water molecules' dynamics is captured via their local translational mobility and by monitoring the auto-correlation function of their dipole vectors.

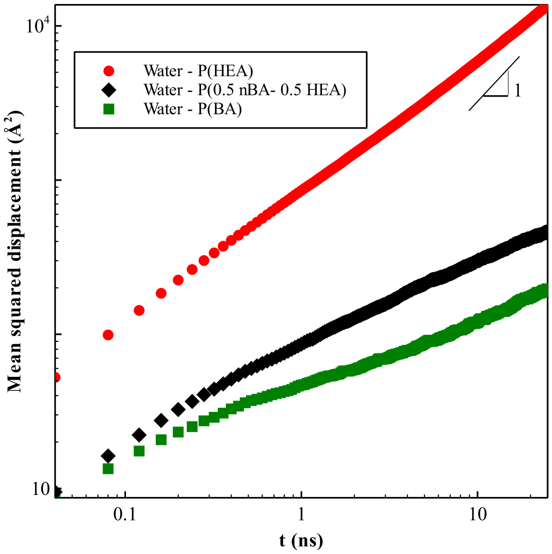

**Figure 2.** Mean-squared displacement of water molecules in three polyacrylates.

## Future Plans

In order to accelerate method development, initial efforts focused on polyacrylate membrane materials due to ease of synthesis. The next round of membrane screenings will target *silicone-based copolymer membranes*, rather than polyacrylates. Like the polyacrylates, silicones are amenable to our combinatorial synthetic techniques and computational methods, but existing literature on pervaporation membranes suggests they may offer better permeability selectivity and higher transport rates for alcohols.

## Broader Impact

Our DMREF involves training a diverse group of young Ph.D. candidates (5) and undergraduate researchers (4), including underrepresented persons, to equip them with the research skills needed in the future workforce in the materials and renewable energy fields. Results from this work are being disseminated to researchers in the bioenergy and materials research fields via professional meetings, while journal publications and a database of membrane materials (under development) will make the work available for education of the general public.

## Data Management and Open Access

An open-access utility is being developed which relies upon the LAMMPS package[1]. Membrane polymers of variable composition can be prepared using the simulated annealing optimization technique by adopting a minimum bond connectivity path of the reacting mixture. Our code can create any polymer structure that follows an addition polymerization pathway using a reacting mixture data file and a parameter file. A manual for using the code is also being prepared to describe the details of the parameter file and the logic of the program.

## References

1. S. Plimpton, *Fast Parallel Algorithms for Short-Range Molecular Dynamics*. J. Comput. Phys. *117*, 1-19 (1995).

## Publications

1. L. Ma, R. Godbole, M. Doerfert, P. Williams, and R.C. Hedden, *A Combinatorial Approach for Tailoring Selectivity and Permeability in Polymeric Pervaporation Membranes*, ACS Comb. Sci. (Submitted) (2015).

# Design and Testing of Nanoalloy Catalysts in 3D Atomic Resolution

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**Keywords:** alloy nanostructures, reactivity prediction, atomic resolution imaging, biomimetic synthesis, force field development

## Project Scope

The project involves an integrated approach of synthesis, 3D characterization, and multi-scale simulation of metal alloy nanostructures to improve the catalytic efficiency of the oxygen reduction reaction (ORR) in fuel cells. The focus is on Pt-M and Pd-M nanoalloys (M=Fe, Co, Ni, Cu, Cr, Mn) that are synthesized using bioinspired surfactants. Multi-scale simulations aim at correlation of computer predictions of ligand-directed alloy shape and internal morphology with cutting edge measurements by equally sloped tomography to discover atomic ordering principles, accelerate experimental activity testing approaches, and suggest new catalyst designs. Improved interatomic potentials and theory will support composition and performance design.

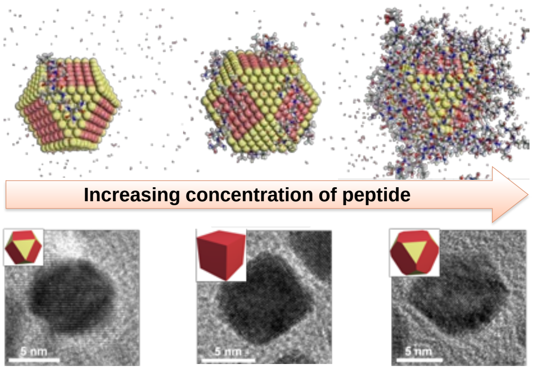

**Figure.** Peptide coverage of nanostructure-bounding facets determines growth directions of nanocrystals, shape, and reactivity. Concentration-dependent changes were tracked by MD simulation and HRTEM [1].

## Relevance to MGI

The team of three PIs will synthesize new nanocatalysts using biomimetic approaches (Huang), image the positions of all atoms in 3D resolution using the world's most powerful electron microscope (Miao), and carry out performance tests in fuel cells in a close feedback loop with predictions by multi-scale modeling and simulation (Heinz). Fundamental understanding of synthesis controls, atomic-scale order, and associated reactivity of the nanoalloys driven by simulation will lead to rational design rules to optimize catalyst performance (ORR, hydrogen oxidation). The development and validation of predictive multi-scale simulation tools further benefits the computational user community and improvements of related materials.

## Technical Progress

The mechanism of selective peptide recognition of Pt nanocrystals and peptide-directed growth into specific shapes has been explained using large-scale molecular dynamics simulation and experiment [1]. The adsorption strength of the peptides depends on the spatial location on the surface and on the peptide concentration in addition to the actual peptide sequence (Figure). Quantitative correlations between preferences in facet coverage and binding energies with nanocrystal shape, size, and yield have been elucidated that can be helpful for the rational design of more complex structures. Currently, the role of peptides in assembling nanoparticles into 3D superstructures is investigated, showing that specific peptides such as T7 can form structures similar to antiparallel beta strands to line up nanoparticles in an orderly fashion. In addition, cubes of Pd-Au alloys were synthesized and the performance in the hydrogen oxidation reaction is currently studied. Several metal and alloy nanoparticles have also been characterized in atomic resolution by equally sloped tomography and provide the first test systems for molecular simulations to understand atomic ordering, improve interatomic potentials, and develop reactive force fields for predictions of catalytic performance.

## Future Plans

Planned work involves the deterministic synthesis of Pt-M and Pd-M nanocrystals (M=Fe, Co, Ni, Cu, Cr, Mn), guided by molecular simulation, the three-dimensional characterization of nanoalloy catalysts at atomic resolution and model refinements, as well as the prediction, testing, and optimization of catalytic activity. The focus in synthesis will be initially on unconventionally shaped alloy nanocrystals bound by high index facets and then shift to specific shapes using simulation-based specifications to maximize rates in ORR and hydrogen oxidation. Liquid-cell imaging and kinetic Monte Carlo simulations will be employed to monitor biomimetic crystal growth. The resulting nanostructures will be characterized by equally sloped tomography using the presently most advanced electron microscope (TEAM I) at the National Center for Electron Microscopy (NCEM at LBNL). The systematic characterization of all atomic species, facets, and shapes will provide key information for reactivity measurements and predictions in catalysis using ab-initio and reactive molecular dynamics simulation (using CHARMM-INTERFACE). Also, correlations between the observed structures and the reliability of current interatomic potentials to predict alloy nanostructure and thermodynamic stability (EAM, INTERFACE) will be explored to result in eventual improvements. Finally, the catalytic activity of the nanoalloys will be tested using voltammetry, measurement of kinetic currents and turnover rates, as well as through in-situ XAS and XPS to monitor changes in nanostructure and possible oxidation states during the reactions. The results, computational and experimental, then enable the development of new theory and guided designs of nanocrystal compositions and shapes for higher efficiency, followed by further synthesis, characterization, and testing.

## Broader impact (Optional for DOE grants/FWPs)

The multidisciplinary, collaborative environment where theory and computation guide and complement the selection, synthesis and characterization of nanoparticles with high catalytic activity will offer a unique training experience for graduate students, undergraduate students, and outreach participants. The team will pay particular attention to recruit students from underrepresented groups and currently includes a minority PhD student at U Akron. Undergraduate students will be supervised as part of the REU program and the Center for Excellence in Engineering and Diversity (CEED) program at UCLA. The PIs will also participate in an annual Engineering Career Day for High School students, teachers, and parents (U Akron), the annual Research Experiences for Teachers program (UCLA), the High School Summer Research Program (UCLA), as well as the coordination of the ACS Chemistry Olympiad for the Akron local section, which includes hands-on laboratory studies for selected High School students.

## Data Management and Open Access

Accurate force fields and new computer codes will be disseminated via NanoHub, the NIST atomistic potentials repository, Heinz’s research webpage, and the Accelrys/Biovia community site to reach a broad user and developer community. Original data on nanocatalyst structure from equally sloped tomography as well as structural models will be fully disclosed in publications as part of the Supporting Information. All other experimental and computational data related to the project will be well organized for long-term storage including backups.

## Publications

1. H. Ramezani-Dakhel, L. Ruan, Y. Huang, and H. Heinz, *Molecular Mechanism of Specific Recognition of Cubic Pt Nanocrystals by Peptides and of the Concentration-Dependent Formation from Seed Crystals*, Adv. Funct. Mater. 2015 (accepted).

# Efficient Methods for Computing High-Accuracy Non-Covalent Interaction Energies in Clusters, Liquids, and Molecular Crystals

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**Keywords:** Non-Covalent Interactions, Intermolecular Interactions, Electronic Structure Theory

## Project Scope

This project aims to develop, implement, and test new algorithms for accurate yet efficient calculation of non-covalent interactions in large systems. Target accuracy is ~1 kcal/mol with respect to the best available correlated wavefunction benchmarks for small systems, but based on a fragmentation approach that is inherently scalable to large non-covalent assemblies (crystals and liquids). Accuracy is assessed based on benchmark comparisons, while efficiency can be judged based on timings and scalability plots with respect to traditional (supersystem) quantum chemistry methods.

## Relevance to MGI

Validation against high-level *ab initio* benchmarks demonstrates that accurate relative energies of different cluster isomers can be predicted at substantially reduced cost, which is the first step toward predicting accurate energies of different structural polymorphs, and to performing condensed-phase simulations. Comparison to experimental enthalpies and free energies of association, in both the gas phase and in room temperature solution, demonstrate an accuracy that is comparable to that inferred at $T = 0$ based on comparison to wavefunction calculations, once reasonable (but relatively simple) entropic corrections are included.

## Technical Progress

We have taken a two-pronged approach to the quantum chemistry of non-covalent interactions: (1) development of an "extended" version of symmetry-adapted perturbation theory (XSAPT) in which monomer-based self-consistent field calculations are combined with a perturbative (and embarrassingly parallelizable) description of intermolecular interactions; and (2) many-body expansions that decompose the total energy into a sum of monomer, dimer, trimer… energies of small fragments, that can again be computed in an embarrassingly parallelizable manner.

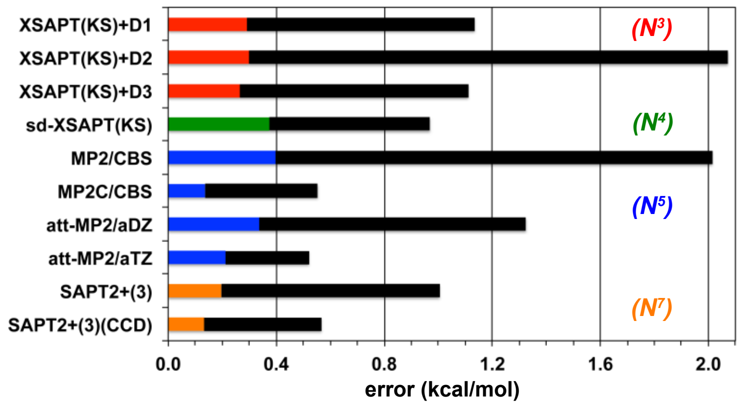

**Figure 1.** Error statistics (vs. CCSD(T)/CBS results for S66) for a variety of quantum chemistry methods. Shown are the mean absolute errors (colored bars, color-code according to how cost scales with system size) as well as the maximum errors (black bars).

On the XSAPT front, we have made significant progress on a method called XSAPT(KS)+D, which combines Kohn-Sham DFT for the monomers with SAPT for the intermolecular interactions, but with empirical atom–atom potentials for dispersion (+D). This is in recognition of the fact that second-order perturbation theory does not afford benchmark-quality results for systems where dispersion is significant. Dispersion potentials can be parameterized in a fully *ab initio* way by using high-order SAPT to extract *ab initio* dispersion potentials for a training set of dimers. Results in Fig. 1 show that our third-generation version of this method, XSAPT(KS)+D3, affords a mean accuracy of 0.3 kcal/mol with respect to CCSD(T)/CBS benchmarks, and a maximum error of about 1 kcal/mol. These are gas-phase, $T$=0 calculations, but in collaboration with Dan Chipman at Notre Dame we are benchmarking these methods against experimentally-measured, room-temperature solution-phase binding affinities (using continuum treatments of the solvent development by Chipman) and, separately, against gas-phase binding free energies that are inferred from cluster ion spectroscopy. Preliminary results suggest that sub-kcal/mol mean accuracy is preserved, using simple continuum and monomer-based DFT treatments of the entropic contribution to $\Delta G$.

With regard to the many-body expansion, our recent results have pointed to some key challenges associated with this widely-used technique, which forms the basis, for example, of the popular Fragment Molecular Orbital method. Specifically, it is not entirely clear that the many-body expansion is convergent, a fact that has been overlooked in most previous studies because (prior to our work) there has been no effort to systematically benchmark this method in *large* systems, using against *high-accuracy* benchmarks (preferably CCSD(T)/CBS). For systems that are much larger than those used in previous benchmark studies, four- and even five-body terms remain significant and are not substantially diminished by popular electrostatic embedding approaches; this leads to serious loss-of-precision problems due to the staggering number of fragment calculations that are required, and is only feasible in pilot studies even when parallelized over hundreds of cores. Results obtained with large basis sets and/or many-body counterpoise corrections (both of which are unusual in most applications of the many-body expansion) suggest that much of this behavior is an artifact of basis set superposition error, and we are currently pursuing ways to avoid this.

**Future Plans**

On the XSAPT front, we are currently working to establish the accuracy and utility of this methodology in realistic applications, in particular the binding of small ligands to macromolecules and molecular scaffolds. This is a collaborative effort with Profs. Lee Woodcock and Brian Space at the University of South Florida, in which enhanced sampling techniques based on Bennett's Acceptance Ratio, developed by the Woodcock group and driven by MD simulations with a low-level method (force field), are combined with accurate, high-level energetics from XSAPT. With Prof. Space's group, we are interested in applying this methodology to metal-organic frameworks, as a means to assist in force field development. This will be facilitated by an implementation of the (X)SAPT method in the atomic orbital (as opposed to molecular orbital) basis, currently underway in the PI's group, which will significantly reduce the memory requirements for calculations involving large fragments, as may be necessary in materials science applications. We are also exploring alternatives to the empirical +D dispersion potentials. Such alternatives include the Tkatchenko-Scheffler method for computing on-the-fly, *ab initio* $C_6$ coefficients, and also methods that compute the dispersion energy based on frequency-dependent polarizabilities for the individual fragments. (The latter approach is what is done in the so-called SAPT-DFT and "coupled MP2" methods.)

In the context of the many-body expansion, we are in the process of obtaining a set of relative energy benchmarks, extrapolated to the basis-set limit, for large molecular clusters. This will enable a more incisive examination of the effects of basis set superposition error. Recognizing that many-body terms beyond trimers may be necessary to achieve benchmark accuracy, we are testing a variety of low-cost, on-the-fly screening procedure that will allow us to throw out many insignificant fragment calculations *a priori*; preliminary tests on water clusters suggest that as many as 85% of the four-body calculations can be eliminated in this way, without loss of accuracy. Analytic gradients for simulations have already been formulated (as have analytic Hessians for vibrational frequencies), and implementation of periodic boundary conditions is planned. An alternative formulation of the many-body expansion that relies on overlapping fragments (*i.e.*, an overlapping tessellation of the supersystem), developed in our group in a manner that generalizes several related approaches, shows promising accuracy at the *two-body* level, which sidesteps many of the problems with four- and higher-order expansions, although the number of dimers is significantly larger when overlapping fragments are employed. We are working to benchmark this approach in large systems in the way that we have done for the non-overlapping apporach, and to implement thresholds.

### Broader impact (Optional for DOE grants/FWPs)

Funds from this grant have so far been used to support three Ph.D. students (with a fourth who will be supported beginning in January 2015). One Ph.D. student supported by this grant has graduated, is currently a postdoc at Georgia Tech working on implementing the many-body expansion into the open-source Psi4 code. A second student will graduate soon. Both of these students will ultimately be pursuing academic jobs. Collaborations have been established with two other DOE-funded PIs (Dan Chipman at Notre Dame and Lee Woodcock at the University of South Florida). The PI recently gave a webinar describing the XSAPT methodology, which is available here: https://www.youtube.com/watch?v=bkAQnFkrUKY&feature=youtu.be. A short online presentation for the Journal of Physical Chemistry Letters is also available, which describes our work on the many-body expansion (see http://pubs.acs.org/iapps/liveslides/pages/index.htm?mscNo=jz401368u).

### Data Management and Open Access

Our many-body expansion and generalized many-body expansion methods are based on a stand-alone, open-source code that acts as a driver for an electronic structure program. (Currently, we use it to drive Q-Chem calculations, but it could be trivially adapted to drive, *e.g.*, NWChem, GAMESS, or Psi4.) Our XSAPT procedure has been implemented in Q-Chem, but we plan to port this method to the open-source Psi4 package, where was can take advantage of a highly efficient implementation of SAPT by David Sherrill's group. (Thus, what is needed is to port the monomer-based "XPol" self-consistent field methodology.)

### Publications

1. K. U. Lao, R. Schäffer, G. Jansen, and J. M. Herbert, *Accurate description of intermolecular interaction energies in ionic systems using symmetry-adapted perturbation theory.* Journal of Chemical Theory and Computation (submitted).

2. K. U. Lao and J. M. Herbert, *Accurate and efficient quantum chemistry calculations for noncovalent interactions in many-body systems: The XSAPT family of methods*. Journal of Physical Chemistry A (DOI: 10.1021/jp5098603).

3. A. F. Morrison, Z.-Q. You, and J. M. Herbert, *Ab initio implementation of the Frenkel-Davydov exciton model: A naturally parallelizable approach to computing collective excitations in crystals and aggregates.* Journal of Chemical Theory and Computation **10**, 5366 (2014).

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11. R. M. Richard and J. M. Herbert, *Many-body expansion with overlapping fragments: Analysis of two approaches*. Journal of Chemical Theory and Computation **9**, 1408 (2013).

# Mechanics of Three-Dimensional Carbon Nanotube Aerogels with Tunable Junctions

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**Keywords:** nanotube network, junction characteristics modulation, mechanical properties.

## Project Scope

The goals of this research program are to combine experimentation with simulation to develop a systematic and comprehensive understanding of how the mechanical properties of single-walled carbon nanotube (SWCNT) aerogels, *i.e.,* three-dimensional (3D) networks of SWCNTs, depend on pore geometry, pore size distribution, and the characteristics of the junctions between nanotubes to improve the performance and to predict an optimal design of SWCNT-based porous structures.

## Relevance to the MGI

In this project, we are developing a 3D mechanical model for SWCNT aerogels that includes realistic network structures as well as nanotube and junction properties that approximate experimental systems. We are then using this model to predict the mechanical properties in compression, including modulus and hysteresis, as a function of network and junction parameters. Our goal is to computationally survey the range of available SWCNT aerogel properties in order to provide insight and guidance to accelerate development of these technologically significant materials.

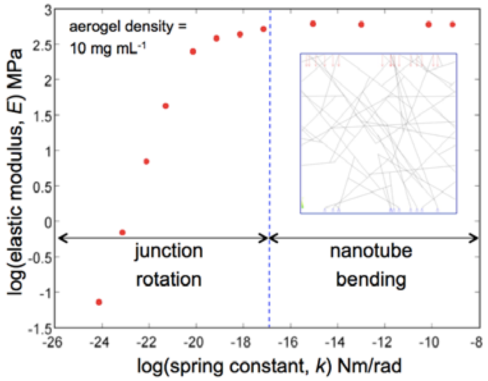

**Figure 1.** Elastic modulus versus junction strength for 2D SWCNT networks. Inset shows the network structure and loading.

## Technical Progress

Develop a 3D mechanical model for SWCNT aerogels (Holm). To model a 3D network of interconnected fibers, we adopt methods used for 3D cellulose networks (*i.e.,* paper). While cellulose fibers are long and compliant and the joints between them are rigid, SWCNTs are relative short and stiff and are connected by deformable joints,; thus, details of the implementation are conceptually and numerically different. We begin by developing the numerical framework in two-dimensions (2D) with SWCNTs represented as beam elements and the nanotube junctions as torsional spring elements. To build a 2D random network of SWCNTs, nanotubes of unit length are placed at random in the simulation cell to achieve the desired density. Any clusters of nanotubes that do not connect to the percolating cluster are eliminated, as their presence numerically destabilizes the system. Finally, junctions are identified, and all dangling ends are removed. The network is then deformed in compression. As shown in Figure 1, we find two elastic deformation regimes: For weak junctions, elastic modulus varies linearly with junction strength, but for sufficiently strong junctions, elastic modulus becomes constant and depends on nanotube stiffness.

Complementary molecular dynamics (MD) simulations of the van der Waals interactions between nanotubes indicate that the most stable nanotube configuration beyond close proximity is crossed instead of parallel, which suggest that nanotube network should resist bundling under compression as is observed in experiments.

Fabricate 3D nanotube networks with diverse junctions (Islam). Our experimental approach has primarily been split into two steps, with the first step being modification of the nanotube network surface with reactive groups and the second step being joining these reactive groups with a suitable linker. The first step has led us to use two chemistries, primarily carbene chemistry and diazonium chemistry, both of which have high efficiency towards modifying the nanotube surface as well as leaving a reactive group on the nanotube surface that allows for further chemical modification. Our efforts in the second step have primarily been focused on the use of polyethylenimine (PEI) as a polymeric crosslinker. Initial tensile mechanical tests show that the PEI crosslinking of nanotube networks improves network tensile modulus by ~400% over the same of uncrosslinked networks.

### Future Plans

Computational activities will focus in two areas, with the overall goal of enhancing the connections between models and experiments:

1. Extend the current 2D mechanical network model to 3D networks. Because 2D and 3D random networks have fundamentally different topologies, this will entail developing a new network generation methodology based on gelation phenomenology. The resulting 3D network structures will be incorporated in the torsional spring model for mechanical analysis.
2. Probe nanotube junction properties via atomistic simulations. Because the properties of nanotube junctions are not well-characterized either experimentally or computationally, we extend the MD approach, and supplement it with electronic structure calculations as necessary, to study other junction structures, including covalently bonded and graphene coated junctions.

Experimental activities will focus on:

1. Optimization of chemical crosslinking of nanotubes at the nodes. Since polymers are capable of wrapping the nanotubes and aiding tensile strength without chemical crosslinks, we will perform a more thorough chemical characterization to ensure crosslinking as well as use different polymerization techniques that would not result in tube wrapping and occlude the mechanical results.
2. Develop understanding of reinforcements from graphene coating of nodes. We have recently discovered that reinforcing the node structure with few-layer graphene, nanotube network can completely recover from compressive strains of over 80% with no observed fatigue. This sharply contrasts the unreinforced SWCNT aerogel, which undergoes plastic deformation at 9% strain, and sees fatigue at even lower strains. We will perform detailed experiments testing the limits and nuances of this physical crosslinking, along with the simulations proposed, to explain this radical improvement in mechanical properties, and create a model system that can be used to improve other porous materials with analogous modifications.

### Broader impact

Two graduate students are being trained in computational and experimental materials science. The computational work has been presented at Materials Science and Technology 2014. Results of this project were incorporated in undergraduate and graduate courses at Carnegie Mellon University, as well as in two K-12 outreach activities. In addition, the PI chaired the First TMS Summit on Creating and Sustaining Diversity in the Minerals, Metals, and Materials Professions (DMMM1).

### Data Management and Open Access

All computational simulations are performed using open access code platforms (ANSYS for finite element calculations, LAMMPS for MD simulations). Full experimental and computational data sets, including metadata such as input decks and initial structures (computation) or conditions and protocols (experiment), will be included as online supplemental information in all publications resulting from this work. In addition, all codes and data are archived at CMU via a GitHub instance and available upon request.

# Iterative Theoretical Morphology Prediction, Synthesis, and Characterization of Novel Donor Oligomers for Accelerated Materials Discovery

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**Keywords:** morphology, charge-transport, structure-property, multiscale, discotic.

## Project Scope

Our theory-synthesis-device team establishes methods to predict organic photovoltaic (OPV) donor molecular structure and morphology, synthesizes new molecules, and tests these in devices. We are studying new oligomers, including a novel type of 2-D trefoil discotic oligomer, and new device architectures. Quantum mechanical (QM) calculations lead to predictions of model crystalline states, and molecular dynamics (MD) calculations simulate morphologies and properties of thin films and BHJ devices. Synthesis of promising new candidates is followed by measurements of device properties. Success is measured by the correspondence between prediction and experiment and by increases in device PCE.

## Relevance to MGI

Morphology prediction is combined with synthesis and device testing to accelerate the discovery of more efficient OPV devices. Using QM and MD simulation methods, we build up morphology predictions and then use them to calculate hole mobilities. New oligomers, including novel discotic trefoil donor molecules, are being synthesized and will be combined with fullerene acceptors for testing in OPVs. The results of these experiments will guide future designs.

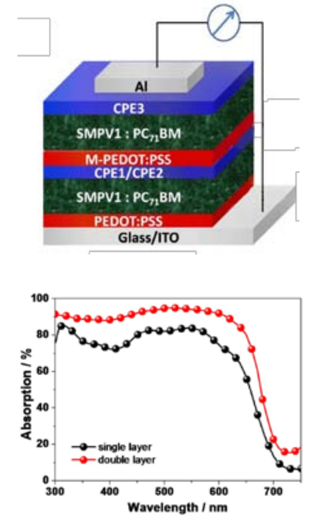

**Figure 1.** (Top) Layer structure of the homo-tandem device. (Bottom) absorption spectra of the single layer device (in black) and homo-tandem device (in red), showing stronger absorption.

## Technical Progress

We developed a homo-tandem OPV device based on the small-molecule donor molecule, SMPV1,[1] later renamed DOR3T-TBDT. The homo-tandem cell (**Figure 1**, top) consists of two identical active layers separated by an interconnecting layer made up of conjugated polyelectrolytes. The homo-tandem cell doubles the optical thickness of the film to increase the number of photons absorbed. In optimized homo-tandem cells of DOR3T-TBDT with an additive, polydimethylsiloxane (PDMS), mixed with an electron-accepting fullerene derivative, PC$_{71}$BM, power conversion efficiency (PCE) reaches 10.1% (vs. 8.0% in the conventional device). Due to strong and broad absorption (**Figure 1**, bottom), films of DOR3T-TBDT achieve good short-circuit current density ($J_{sc}$) of 12.5 mA cm$^{-2}$. In high-resolution transmission electron microscopy (HRTEM) images, it is seen that the addition of PDMS changes the morphology of the original device to produce smaller domains with a greater number of well-defined charge transport pathways. QM calculations show that the calculated band gap for DOR3T-TBDT matches experiment only if the conjugated backbone is constrained to be nearly planar; thin films geometries of DOR3T-TBDT are, therefore, different from the gas phase geometry of the monomer.

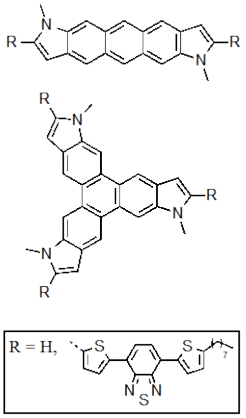

**Figure 2.** New oligomers.

Perovskite materials have produced solar cells with over 20% efficiency, but suffer from performance degradation and poor near-infrared spectral absorption. An OPV device that integrates perovskite material with a low band-gap oligomeric BHJ material (DOR3T-TBDT) achieves a high $J_{sc}$ of 21.2 mA cm$^{-2}$ and a PCE of 14.3%.[2] The analogous perovskite-only device achieves a $J_{sc}$ of 19.3 mA cm$^{-2}$, confirming improved absorption and photon conversion by the BHJ film.

We have developed computational methods for predicting hole mobilities in thin-films.[3] For a test set of 22 conjugated small molecules for which hole mobility data have been measured for crystals and thin films, we have calculated both single-crystal and thin-film hole mobility with good agreement with experiment. We incorporate varying levels of morphological disorder using MD simulations and then kinetic Monte Carlo time-of-flight analysis to calculate hole mobilities. With these methods, we computed predicted domain morphologies of DOR3T-TBDT with MD and performed charge transport analysis on them to find unexpectedly high hole mobilities. Morphologies from these planar layers are under further study using MD. Additionally, we have studied charge transport in a family of a didodecyl-quaterthiophene polymer (PQT-12) and monomer, dimer, and trimer oligomers (DDQT-1, -2, and -3) of the polymer developed by the Briseno group.[4] We predict morphology disorder parameters for the oligomers that are in close agreement with the experimental value for the polymer.

## Future Plans

The development of a device with over 10% PCE made from a single donor molecule, DOR3T-TBDT, suggests that the homo-tandem concept can be used to create devices with even higher efficiency. Morphology at BHJ interfaces will be studied to advance predictability of PCE in OPVs. Typical OPV donor molecules are constructed on a linear backbone, and we will explore the diindoles (**Figure 2**, top) to determine how a switch of a benzene ring to a pyrrole influences electronic properties. We focus on a new 2-D arrangement present in discotic trefoil oligomeric OPV donors (e.g., **Figure 2**, middle). Similar molecules common to liquid crystals pack in columnar layers with high hole-mobility values. Several core subunits have been synthesized, and the syntheses of complete oligomers including the core triindole triply substituted with pendant donor/acceptor side chains (Fig. 2, bottom) are in progress. The oligomers will be compared computationally and experimentally to linear analogs to determine how the 1D vs. 2D architectures influence electronic structure and packing morphologies. Cores and oligomers will be fabricated and tested in devices for feedback to synthesis and computation. Modified structures will be designed and tested.

## Broader impact

The participants have all been involved in undergraduate mentorship and collaborations with groups outside of UCLA. Zhongtian Mao was a visiting student from Fudan University in Shanghai as part of the UCLA CSST program. During this past summer, Zhongtian became versed in a variety of computational chemistry software to study electronic structure, morphology, and charge transport in DOR3T-TBDT. Nate Druckerman is a senior at UCLA participating in building a library of conformational preferences of oligomeric organic semiconductors. We have developed research collaborations with groups outside of UCLA; the Houk group actively collaborates with Alejandro Briseno at UMass Amherst and the Yang group has collaborations with Valy Vardeny at Utah.

## Data Management and Open Access

Our results are disseminated by published work and conference presentations. Our labs have published several hundred manuscripts over the past 5 years, and are eager to share scientific results. Our results have been presented through lectures (>200 invited lectures since 2008). This practice will be continued, and laboratory websites will be maintained to showcase our studies and associated publications.

## Publications

1. Y. Liu, C.-C. Chen, Z. Hong, J. Gao, Y. (M.) Yang, H. Zhou, L. Dou, G. Li, and Y. Yang, *Solution-processed small-molecule solar cells: breaking the 10% power conversion efficiency*, Scientific Reports **3**, 3356 (2013).
2. Y. Liu, Z. Hong, Q. Chen, W. Chang, H. Zhou, T.-B. Song, E. Young, Y. Yang, J. You, G. Li, and Y. Yang, *Integrated Perovskite/Bulk-Heterojunction toward Efficient Solar Cells*, Nano Letters, manuscript just accepted. DOI: 10.1021/nl504168q
3. I. Yavuz, B. N. Martin, J. Park, and K. N. Houk, *Theoretical study on the molecular ordering, paracrystallinity and charge-transport parameters of oligomers in different crystalline phases*, J. Am. Chem. Soc., submitted and in revision.
4. I. Yavuz, L. Zhang, A. L. Briseno, and K. N. Houk, *Simulations of Molecular Ordering and Charge-Transport of Oligo-Didodecylquaterthiophenes (DDQT)*, Journal of Physical Chemistry C, manuscript just accepted**.** DOI: 10.1021/jp510567d

# Real Time Control of Grain Growth in Metals

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**Keywords:** Grain growth control, temperature control, Phase Field model, Monte Carlo method, SEM

**Project Scope:** This proposal focuses on developing the methodology and algorithms necessary to actively control materials processing to achieve a target microstructure. We anticipate our major contribution to be the synthesis of experimental characterization, process control, and microstructure simulation to predict, monitor and control microstructural evolution during materials processing. In this project we focus on thermal processing of polycrystalline metals, specifically control of grain growth in Cu, but the methods we develop should be extensible to a broader range of processing parameters.

**Relevance to MGI:** The macroscale engineering properties of metals, such as ductility, strength, and fatigue resistance, are directly linked to microstructural characteristics, which, in turn, are generated during thermo-mechanical processing. Thus, active control of the processing conditions, through iterative cycles of processing, measurement, modeling and feed-forward /feed-back control, to create a desired microstructure and resulting macroscale properties is a major priority for materials manufacturers and for the MGI.

**Technical Progress:** Our two over-arching project goals are (i) To enhance predictive capability for the relationship between thermal processing and microstructure in polycrystalline metals. This is enabled through coupling of in situ real time observation with simulation of microstructural evolution, across multiple temporal and spatial scales, as functions of thermal trajectories; and (ii) To subsequently control microstructural evolution by regulating the temperature distribution using model-based feed-forward control and measurement-based feedback control. This approach requires simultaneous progress on multiple scientific and engineering fronts. 1) We have developed a ten zone multi-zone resistive heater, upon which the polycrystalline metal films of interest are deposited, and that can be operated within a scanning electron microscope (SEM) with independent control of different heating zones, Figure 1. The design of this heater array targets temperatures in the range 350 – 450$^o$ C, partly through raising of the base temperature to 200-300$^o$C from an SEM heating stage, and partly through controlled temperature excursions in each zone, defined by individual Ti microheater strips for each zone. This enables programmable temperature distributions across the sample area. The thermal design of the heater array has been enabled through extensive finite element analysis (FEA) modeling. 2) Within the SEM, we will apply novel real-time characterization methods to simultaneously measure microstructure and temperature (the latter using diffuse scattering from electron backscattered diffraction patterns), in order to study the microstructural response to controlled sets of inputs to the multi-zone heater and resulting temperature fields, and to compare the observed evolving microstructure to predictive models. Extension to 3D imaging and correlation of 2D-3D grain models will be enabled through tomographic imaging in a focused ion beam. Characterization of Cu grain structure using both electron and ion beam imaging, as well as development of algorithms for automated grain identification and analysis, is underway. 3) Detailed continuum (phase field) and Monte Carlo grain growth models are being developed to predict both microstructural trajectories as functions of time and temperature, and the local dependence (gradient) of microstructure upon time and temperature. 4) From a combination of simulations and experimental data, the sensitivity of microstructural characteristics, e.g. grain size distribution, to heater settings will be characterized. From these sensitivities, using inverse problem solving techniques, we will predict and confirm the optimal heater setting histories to obtain a prescribed microstructure. 5) The combined information from modeling and real time observation (and specifically triggered by deviations between the two), will then be used in a combined feed-forward and feedback control strategy for real-time control of microstructure evolution. Initial control strategies have been developed for feed-forward control of the desired temperature distribution of FEA models of the heater array, by solving the inverse problem for a constant heat input. 6) The estimator and controller design, particularly for the feedback loop, depends on model fidelity, sensor noise, and timing (when and how often is the heater control adjusted). We are posing this as an optimization problem, by select the control strategy and sampling times to steer the expected value of microstructure towards the goal in the presence of model uncertainty. Figure 2 shows the FEA simulation under temperature feedback control to account for modeling errors, and process noise and disturbance. The feedback gain is chosen based on a graph interconnection of the output temperature measurements. The graph structure and the feedback gains are chosen to minimize spatial temperature gradient during the transient phase. We are currently implementing the first generation hardware control strategies, using independent control of each heater zone current, and using the calibrated resistivity as a function of temperature of each Ti heater line as the set of control variables to implement desired temperature distributions across the heater array.

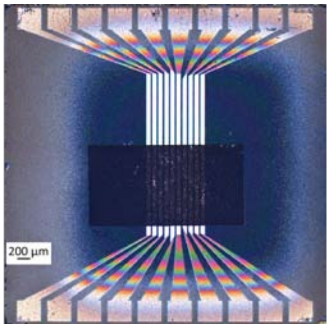


***Figure 1.*** *Optical image of ten element heater array*

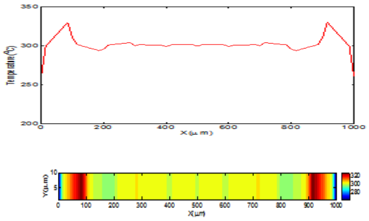
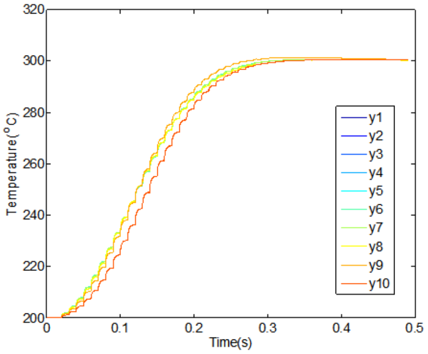


***Figure 2.*** *Feedback temperature control with gain chosen to minimize spatial temperature gradient during transient.*



**Future Plans.** Within the next few months, hardware implementation for the feed-forward / feed-back control loop of desired temperature distributions will be completed in-situ to the SEM. Experimental calibrations of temperature distribution to grain size / orientation distributions will then be developed. Monte Carlo based grain growth models coupled to the temperature evolution models are under development and together with phase field models will be tested / refined by comparison to experimental data, and incorporated in the control design.

**Broader impact.** A "core body of knowledge" has been defined for the four participating graduate students, combining selected graduate courses and which will be supplemented by a "mini symposium" on the science of grain growth in late January, 2015. Student exchanges, where participating graduate students spend extended period working in other PIs' laboratories are being implemented starting in Spring 2015. Multiple undergraduate students have participated in the project, including contributions to phase field and Monte Carlo simulation development, and development of grain delineation algorithms from experimental images. A project symposium will be held in conjunction with the annual Rensselaer Center for Automation Technology and Systems (CATS) Advanced Manufacturing Conference in April 2015, that attracts many industrial participants.

**Data Management and Open Access.** Relevant simulation and experimental results are shared among team members, and salient data / results stored on the project wiki site. The full team meets biweekly. As project progress develops to the point of data /predictions / control schema that are relevant to the broader community, external access to the wiki will be provided on request. At the conclusion of the project relevant data sets and products will be made permanently available to the external community (research advances and findings will of course also be published in the scientific literature).

**Publications:** (1) Chengjian Zheng, Yixuan Tan, John T. Wen, and Antoinette Maniatty, "FEM Modeling And Temperature Consensus Control of An In-situ Heater Array Designed For Controlling Material Microstructure," submitted to the 2015 American Control Conference. (2) Prabhu Balasubramanian, David Crist, Yixuan Tan, Chengjian Zheng, Robert Hull, Daniel Lewis, Antoinette Maniatty, and John Wen, "Real-time Control of Grain Growth in Metals," Advanced Manufacturing Conference, Troy, NY, April 22, 2014 (poster).

# Computationally guided design of multicomponent materials for electrocatalytic reactions

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**Keywords:** Catalysis, Energy, Nanomaterials, Cascade, Electrochemical

## Project Scope

We will develop multicomponent catalytic materials that allow greater efficiency in energy-demanding reactions. Materials will be prepared by nanoscale synthesis techniques to link functional components to catalyze an overall reaction. Close linking of these material components can reduce the formation of unwanted and environmentally hazardous byproducts and decrease the required energy input for important chemical reactions. Predictive multi-scale models will be developed to guide the design of linking these components. These models will be validated and refined through experimental testing of computational designs. Multi-component catalyst activity and selectivity will be compared with single active site materials.

## Relevance to MGI

An alternative approach to catalytic conversion will be developed using multi-component, multi-active site materials. Communication between active sites will be controlled by the selective transport of energetic intermediates. A computationally-guided design framework will 1) utilize atomistic and electronic structure methods to optimize individual catalytic components, and 2) construct a coupled microkinetic/transport model to guide construction of the multi-component material. Synthesis, fabrication, characterization, and reactivity studies will validate computational models and realize the enhancements offered by the catalysts.

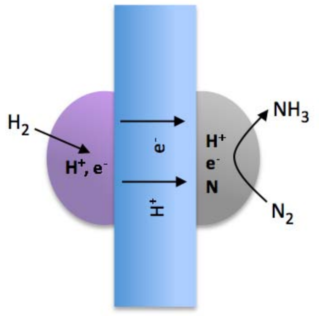

**Figure.** Ammonia synthesis on a cascade catalytic system involving the formation of energetic reaction intermediate ($H^+$+$e^-$).

## Technical Progress

Initial efforts have concentrated on developing the framework for the coupled microkinetic and transport model. This model is initially being applied to a hypothetical A to B to C series reaction, with the intermediate B species passed between catalytic sites. The model will be used to define the individual catalytic and transport properties needed in the multi-component catalyst to exceed the performance of a single-site catalyst.

## Future Plans

Our project team has identified a set of initial focus areas for initiating our work in multi-component catalyst development.

1) <u>Develop the framework for a coupled micro-kinetic and transport model that will guide multicomponent material construction.</u> We will initially use both a hypothetical A to B to C reaction as well as electrochemical ammonia synthesis as test systems to delineate the catalytic properties and nanostructure necessary for the multi-site catalyst to exceed the performance of a single-site material.

2) Collect initial experimental data for oxidative coupling of methane using a two site catalytic system. This initial data will demonstrate the potential for better balancing activity and selectivity concerns in upgrading natural gas to ethane/ethylene in this process, and provide experimental data against which to validate developed models. Electronic structure theory calculations will also be used to explain observed trends in catalyst performance and guide materials selection.
3) Synthesis of Janus particles. Janus particles will be composed of two metal sites that are connected through an interface. We will initially employ two different methods to synthesize these particles: 1) Pickering emulsion method that involves an emulsion system stabilized by colloidal metal particles, which adsorb at the interface between the oil-water phases, and (2) Surface nucleation and growth method which involves the nucleation and growth of particles from one type of metal (yellow particles) on the surface of the seed particles.
4) Develop mechanistic insight into the impact of self-assembled monolayers on nanoparticle catalyst particles. SAM-modified nanoparticles will serve as a building block in multi-component catalytic systems. We will apply electronic structure and reactive force-field methods, in conjunction with ongoing experimental efforts, to explain the mechanistic impact of SAM-modification on catalytic hydrogenation and hydrodeoxygenation of furfural.

## Broader impact

Research efforts will be integrated with educational and outreach activities to broaden the impact of the proposed work. Undergraduate researchers will be integrated into research efforts at the four partner institutions, involving these students in multi-disciplinary work with exposure to our collaborative team. Undergraduate researchers will be drawn from programs that target underrepresented groups, such as Penn State's Women in Science and Engineering Research (WISER) and Wayne State's Michigan-Louis Stokes Alliance for Minority Participation (LSAMP) programs. Research groups at each institution will participate in science outreach activities targeted at preschool through K-12 groups, such as Central Pennsylvania's "Exploration Days" and the Michigan Science Center's "Ask the Expert" series. The formation of our collaborative group and coordinated course offerings among partner institutions will provide opportunities for collaborative teaching, specifically aimed at integrating active learning tools.

## Data Management and Open Access

Developed multi-scale models will be made available on a project website, and when possible, included is online supplementary material in published papers.

# Analysis and Optimization of Polymer Networks for Emerging Applications

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**Keywords:** polymer networks, gels, hydrogels, primary loops, mechanical properties.

## Project Scope

Understanding polymer networks at molecular level is motivated by their broad range of applications. This project aims to develop and test theories for predicting the number of primary loops, the major molecular defects in polymer networks, providing design guidance for the structure, mechanical, and transport properties in these ubiquitous systems. The results of this project will provide new synthetic strategies, experimental methods, computational approaches, and theoretical developments related to the microstructure of polymer networks.

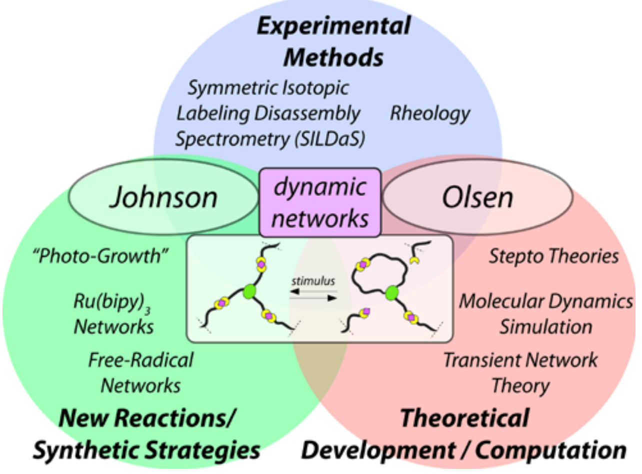

**Figure 1.** This project aims to analyze and predict new properties of polymer networks through the synergistic application of physical characterization techniques, synthetic strategies, and theoretical developments.

## Relevance to MGI

This project has pioneered a new method to directly measure the concentration of loops and bridges in a polymer network using mass spectrometry. This technique provides the ability to fundamentally test theories of polymer gel formation (rate theory and Monte Carlo theory models for gel formation kinetics) and polymer network mechanics (affine and phantom network theories). The work here is synthesizing new network materials, testing their mechanical properties and chain configurations, and using this new data to iteratively test and improve the theories describing polymer networks and gels.

## Technical Progress

Based on the preliminary data presented in the proposal, an advanced analysis method, "Symmetric Isotopic Labeling Disassembly Spectrometry" (SILDaS), has been developed to quantify primary loops in tri-functional model network materials. As aimed, the initial work has been successfully published. Such strategy enable analyzing more universal network system compared to our previously developed concept called "Network Disassembly Spectrometry" (NDS),[1] where an asymmetric macromer (the polymer bridge between two junctions) with restricted molecular weight has to be designed purposefully. Furthermore, in order to simplify the synthetic process, the mass-label macromer was employed to replace isotopically label one. In this case, a new term called "Symmetric Mass Labeling Disassembly Spectrometry" (SMLDaS) is also introduced. The quantification of primary loops was then conducted in a tetra-functional network system and the manuscript is in preparation.

One of our goals in this project is to study the influence and contribution of loops on the mechanical property of polymer networks. However, the crosslinking chemistry employed in our former study encountered various issues for accurate rheological measurement. The tetrazine-norbornene coupling chemistry (used in NDS) releases $N_2$ gas, leading to the formation of trapped bubbles in the gel. The $Cu^I$-catalyzed click chemistry (used in SILDaS) is $O_2$ sensitive which is difficult to conduct on the stage of a rheometer of ambient conditions. Therefore, an air-friendly crosslinking reaction involving Michael-addition of oxonorbornadiene was investigated. In addition, the temperature-prompted retro-Diels-Alder (DA) reaction of resulting adducts provides a cleaner and simpler way for gel degradation.

## Future Plans

The phantom network theory and the affine network theory have both been developed to relate the modulus of polymer networks to the density of elastically effective chains, $\nu$. Both theories predict that the shear modulus of a gel, $G'$, can be quantified by the equation $G' = C\nu kT$, where $kT$ is the thermal energy and $C$ is a constant that has a value of 1 for the affine network model and $1\text{-}2/f$ for the phantom network model, where $f$ is the functionality of network junctions. Unfortunately, the validity of these theories has not been demonstrated experimentally due to difficulty of quantifying $\nu$. The fraction of elastically ineffective chains measured from SILDaS allows us to address this issue and the contribution of molecular defects to mechanical property will be evaluated by rheological measurement. The resulting data will provide experimentally estimated values of $C$, thereby differentiating between the different network models. In order to perform the rheological measurements, 1 mm thick samples will be cast into a Teflon molds and then be punched out to form 12 mm diameter disks and loaded onto the oscillatory shear rheometer using a parallel plate geometry. A series of gels containing various fractions of loops will be synthesized *via* varying the initial concentrations of macromers and crosslinkers and then be swelled to the same final concentrations. Other parameters to be adjusted include the molecular weight of macromer, the functionality number $f$, and potentially the molecular weight distribution of macromer. Macromers employed in this project will be focused on PEG first and extended to other types such as polystyrene (PS) or polydimethylsiloxane (PDMS). Polymer network in a bulk state formed from PDMS macromer will exhibit particular interest due to its rubbery properties, attributed to the subzero glass transition temperature and melting point of PDMS. Crosslinker will also be extended from multifunctional small molecules to macromolecular crosslinker, e.g., chain-end functionalized multi-arms PEG. Accordingly, the matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF MS) will be employed to analyze the latter system for SILDaS.

While existing rate theory and Monte Carlo theories have been able to successfully capture the reaction kinetics and concentration-dependence of loops in polymer networks when the reactive groups are present in a 1 to 1 ratio, experimental data has been generated for networks that have off-stoichiometric reagents, and the rate and Monte Carlo theories pioneered by Stepto[3] and published by the PIs do not capture even at a qualitative level the trends in the experimental data. Therefore, modifications to these theories are being developed that may have the ability to more accurately capture the process of network formation in off-stochiometric systems.

## Broader impact

A deeper understanding of polymer networks at molecular level has the potential to transform our engineering of these ubiquitous materials. It will advance discovery of novel self-healing materials, tunable filtration devices for removal of toxic agents from wastewater, and matrices for cellular and tissue engineering, in addition to having an immediate impact on a myriad of industrial products from coatings to tires.

## Data Management and Open Access

The codes for rate theory and Monte Carlo simulation will be posted on the Olsen group website once the work is published. All data for this project is also being archived on a server which is backed up internally using multiple drives and off-site on a daily basis to provide for data security. Other laboratory data that is not generated digitally is stored in lab notebooks that are archived in the Johnson and Olsen labs.

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# Center for Emergent Superconductivity

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## Project Scope

The CES program aims to establish and use a coherent combination of materials chemistry, computational modeling and fundamental many-body theory to discover new high temperature superconductors (HTS) and to improve the properties of existing HTS phases. This enterprise involves a wide range of expertise and makes use of the most advanced experimental and computational facilities available in the world. The Center brings computational materials scientists, experimental chemists and physicists specializing in synthesis together to work in a close feedback driven loop that directly addresses grand challenges in correlated materials as well as electronic and photonic materials.

## Relevance to MGI

To understand what kinds of structures to aim for, the Center uses Quantum Monte Carlo (QMC) modeling of real materials to derive parameters which are then fed into Dynamical Mean Field Theory (DMFT) based calculations to predict electronic structure. This connection between real materials and desired properties is a crucial part of the approach. To identify the key electronic and magnetic properties that underlie the emergence of HTS, we combine wide ranging experiments that fully characterize the highly correlated electronic systems we synthesize with field theoretic modeling to provide metrics for computational modeling and suggestions for new directions to pursue. To understand how the flux pinning properties of known HTS compounds can be improved by processing, we combine highly controlled nano-processing technology with sub-atomic scale structural and electronic characterization and QMC-based modeling to obtain a quantitative view of how the electronic structure relaxes at interfaces and boundaries.

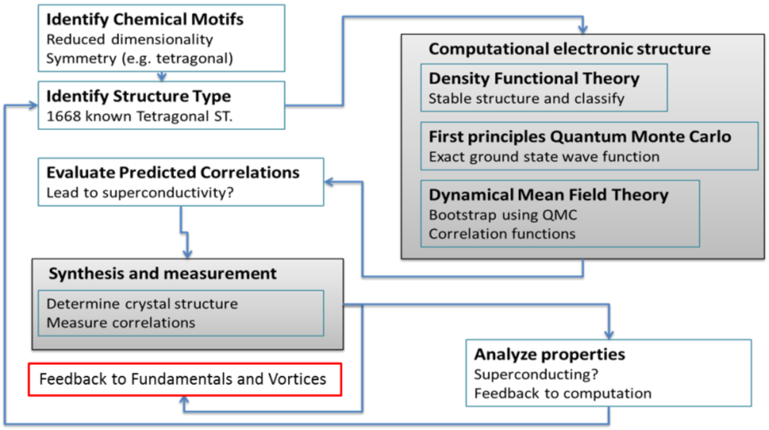

Figure 1. Work flow leading to the discovery of new HTS phases.

## Technical Progress

Our search for new phases is developing evolutionary, self-aware algorithms that shift the use of computing power to more relevant areas of the phase space or higher accuracy electronic structure methods as they are shown to work. The core algorithm of such searches is highly parallelizable as scaling is dependent on the number of candidate structures created in each generation of search. For example, algorithms which adjust the allocation of the computing resources are currently being optimized to use Blue Waters petascale computing for exploring the Ba-Ru-S composition space. This ternary system like other HTS materials has phases in which the electronic structure is derived from covalent bonds. An MGI discovery pipeline for the new phases with properties such as anti-ferromagnetic ordering (AFM) and Fermi-surface nesting is being developed. Phases identified have included the known binary phases and some new ternary phases which have now been promoted for lab-scale synthesis trials. Using symmetry and seed structures as chemical motif, the number of calculations performed using different flavors of density functional theory (DFT) can be reduced significantly from a fully random version. For example, we have increased our bias towards Ru-S square planar motifs and discovered a ternary phase $Ba_2Ru_4S_4$ having a network of edge-sharing $RuS_4$ square-planar layer separated by a Ba layer, with comparable stability to binary $RuS_2$ phase. Synthesis of this and several other phases is currently being attempted.

The materials that exhibit unconventional superconductivity fall into the class of materials called strongly correlated. In this class, modern density functional theories have proven unable to describe their electronic structure because electron correlations are inherently important to their electronic properties. To address this challenge, we are using two advanced many-body methods: ab-initio QMC and DMFT. Each method fulfills a particular role in this project. In the QMC method, we simulate the electron correlations directly using a highly realistic computer model, with only the positions of atoms as input parameters. This technique has been shown to obtain very accurate results on challenging systems without adjustable parameters (see Figure 2). This accuracy comes with a fairly large computational cost, but modern implementations combined with large-scale computational facilities such as the ALCF computer Mira and NCSA's Blue Waters can now enable these calculations to be completed quickly. These developments have opened the way for truly predictive accuracy for the ground state and a few excited states of strongly correlated electron materials; however, the QMC methods currently cannot calculate spectral or transport properties, which are of con siderable interest. Using a model for the microscopic interactions, the DMFT method can predict spectral and transport properties. We are working to use the QMC methods to determine the nature of microscopic interactions, which will then feed into the DMFT solver to find the full gamut of predicted properties.

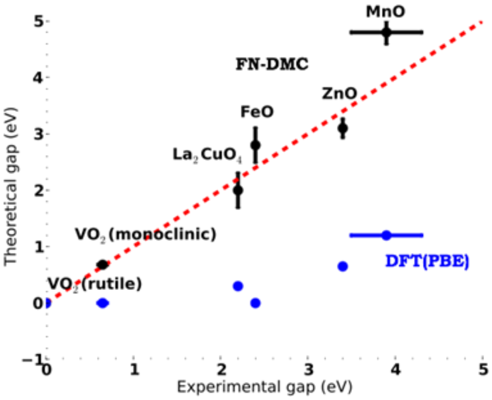

Figure 2. Energy gaps of several correlated materials calculated with diffusion quantum Monte Carlo (DMC) and standard density functional theory (DFT) versus experiment.

Processing can also strongly change the flux pinning properties of HTS materials. The center has been studying how ion damage tracks enable this. The work has resulted in a two-fold improvement in the critical current obtained in state of the art HTS cables. We have studied how this occurs with atomic scale microscopy and spectroscopic characterization. We are also computing the changes introduced locally in the many body superconducting wavefunction by the rapid spatial variation of the damage track.

## Future Plans

We will continue to search for new phases in other covalent systems, looking for two dimensional antiferromagnetically correlated compounds which have high a Neel temperature and which can be doped. This will survey compositions that are known to exist as well as look for new chemical phases that have yet to be discovered. We will combine synthesis with computational prediction. We will explore the use of organometallic precursors in the growth of compounds containing refractory transition metal compounds. This is particularly important because such systems often have very stable binary phases and non-equilibrium routes often enable synthesis of hard to form phases.

**Data Management and Open Access**

We have begun a materials Wiki in which all our synthesis and predictive computational chemistry results can be rapidly made available.

**CES Publications** (since August 2014)

M. P. M. Dean, "Insights into the high temperature superconducting cuprates from resonant inelastic X-ray scattering," J. Magn. Magn. Mater. **376**, 3-13 (2015).

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Garrett Vanacore, Phillip W. Phillips, "Minding the gap in holographic models of interacting fermions," Phys. Rev. D **90**, 044022 (2014).

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# Engineering Strong, Highly Conductive Nanotube Fibers Via Fusion

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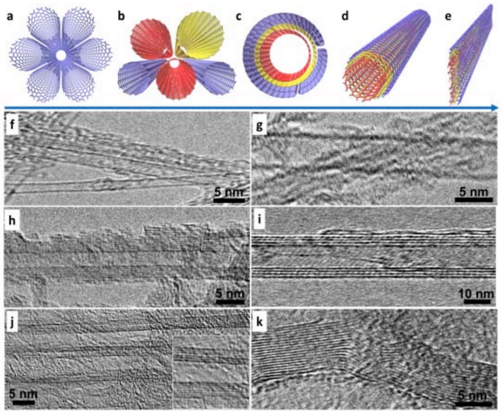
**Keywords:** Carbon Nanotubes, Nano-fibers, Atomistic Simulation, Data Mining, Nanomanufacturing

**Project Scope**: The objective of this project is to create high-performing and multifunctional fibers for applications in aerospace, energy storage, lightweight materials etc. The main challenge of creating such fibers is that they need to excel in more than one area. They should be strong while also being exceptional conductors of heat and electricity. For this, our research focuses on designing and engineering carbon nanotubes (CNT) networks into larger, more seamless structures with excellent performance. The research includes studying the best way to organize the carbon nanotubes into the network, as well as studying the best way to fuse nanoscopic filament together by applying controlled electric voltage across the network. The optimal network organization and electrical fusion process will be identified through experiments and simulations, and by using data mining to understand the complex relationship between how the fused networks are made and how they perform.

**Relevance to MGI**: This project will engage interdependent experimental, simulation, and data mining efforts to enable scalable multifunctional fibers through design and engineering of nanostructures and architectures of CNT fibers. The experimental parameters for electrical fusion, as well as CNT structure, super-assembly process and initial fiber architecture will be studied. Characterization and coarse-grained atomistic simulation of fused fibers will relate physical properties to structure and structure to processing. Data mining will extract the relationship between properties and processing. Therefore the outcome of the proposed activity can be integrated into materials genome initiatives as the ensemble of science, simulation tools, and processes for manufacturing multifunctional fibers offer transformative and revolutionary performance.

**Technical Progress: T**he PI, Jung, reported the preliminary result on which the project is founded, called *Nanotube Fusion*[1]. This highly controllable method controls input voltages in CNT networks to create covalently bonded $sp^2$ molecular junctions between CNTs. It can further transform them into larger diameter SWCNTs, multi-walled CNTs, or multi-layered graphene nanoribbons with improved thermal and electrical conductivities. The project started at September and PIs (Jung and Livermore) are investigating intrinsic structural, mechanical and transport properties of nanotube fibers (spun yarn and roving) supplied by Nanocomp. Inc. A paper on the mechanical behavior of the nanotube fibers prior to fusion was published at the PowerMEMS 2014 conference. Also the PI (Jung) is designing a temperature controlled multi-channels electrical fiber fusion system. PI Kaeli, working with PIs Jung and Livermore, is building a framework to characterize the number and range of properties associated with CNTs. We are developing working *data dictionary* that captures the types and range of properties. This effort will feed into the development of a fiber fusion toolset that allows a designer to specify properties of the desired CNT. The tool will provide guidance on the material properties and manufacturing processes based on experimental measurements and simulation results provided by PI Upmanyu.



**Future Plans**: The combination of superior electronic, thermal, and mechanical properties makes CNT networks an ideal building block for high-performance multifunctional materials, but these advantages are eroded in van der Waals connected networks. If van der Waals interactions were replaced with $sp^2$ bonds to create macroscopic seamless *$sp^2$* carbon nanostructures, performance would increase enormously. Recently the PI developed a novel carbon nanostructure engineering process called *Nanotube Fusion*. This highly controllable method controls input voltages in CNT networks to create covalently bonded *$sp^2$* molecular junctions and seamless *$sp^2$* molecular structure of networks. Harnessing this innovation requires navigating many process and structural parameters. To overcome these challenges, our research plan leverages (1) simulation to predict performance, (2) process engineering to create macroscopic seamless *$sp^2$* carbon nanostructures, and (3) data mining to guide process optimization. The research will offer a transformative result: extremely high-performing, scalable, seamless *$sp^2$* nanostructured fibers together with an understanding of their underlying physics and manufacturing processes. The resulting material will have tremendous implications from a fundamental and an applied perspective. The toolsets being delivered by this project will enable exploration of new materials and allow others to leverage the lessons learned. The proposed research will advance knowledge in the design of simulation tools and of *$sp^2$* covalently-bonded carbon nanomaterials.

**Broader impact:** Our broader impacts include the societal benefits from its well-reasoned plans for enhancing outreach and broadening the participation of students from underrepresented groups across diverse educational levels and backgrounds. Activities for outreach and broadening participation include summer mentoring of high school students in the laboratory, recruiting underrepresented minority undergraduates through the Louis Stokes Alliance for Minority Participation, and recruiting students through Northeastern's Society for Women Engineers and Minority Engineering Program. The PIs will leverage this proposal to i) develop an MRS symposium series on "Multifunctional Nanostructured Networks" and ii) create a seminar series focused on Materials Science in general, in collaboration with several research centers at Northeastern.

**Data Management and Open Access**: The research data are captured using pieces of equipment that in general have their own native data types. Raw data that are of sufficient quality will be processed to extract parameters of interest. The resulting raw and processed data will be stored as well-documented Excel spreadsheets or Matlab files for further analysis. The files will be manipulated in their respective software platforms, but they will be stored in stable formats for long term preservation. The naming convention will include project name, date, and data descriptor. The metadata (what was measured; how, when, why, where, and by whom it was measured) will be recorded in a readme.txt file, which will also refer to individual .txt files in which experimental details for each experiment are recorded. Laboratory processes will be recorded as text and image files as described above. Simulation procedures and the analytical basis for models will be recorded in a permanent fashion by prompt archival publication, ensuring their future accessibility. Simulation tools will be documented while they are being written and stored in their native formats. Data access will be through prompt publication, posting on the investigators' web sites, and Northeastern's Digital Repository Service. Figures, charts, and tables resulting from our analysis of the raw data will be prepared for prompt presentation and publication including both the primary publication and the supplementary materials. The data-mining tools developed in this project, and the database developed as part of this project, will be made available to the research community. The database will be accompanied with a complete data dictionary, and associated database documentation.

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# Network for ab initio many-body methods: development, education and training

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**Keywords:** electronic structure, many-body methods, validation, high-performance computing

## Project Scope

This project links the developers of ab initio many-body electronic structure methods, especially quantum Monte Carlo (QMC) methods, and the developers and users of the open-source QMC package QMCPACK to build a next-generation QMC framework that enables science critical to DOE missions and accelerates discovery of advanced materials. The project specifically supports methods development and applications, aims to foster the collaborations among developers and users, and to educate new computational materials scientists. The intended outcomes include software, efficient workflows, and data repositories as well as scientific applications.

## Relevance to MGI

A grand challenge of quantum mechanical materials modeling is be able to accurately predict the properties of materials without empiricism. This is important for wholly new materials and properties, where no data is available to fit, and for properties and conditions that are experimentally difficult or costly to access. QMC methods are able to achieve this because the methodology is – in principle – systematically improvable, enabling approximations to be tested. Validation is in part performed using standard test sets and established material properties. E.g., in [7] we validated QMC on a range of molecules and solids prior to application to a more complex system where QMC becomes the benchmark. (Figure 1).

## Technical Progress

Although in principle systematically improvable, QMC calculations in practice typically involve a number of choices that introduce systematic errors. These errors are often due to the use of pseudopotentials (although all electron calculations can be performed) and the assumption of a particular nodal surface for the trial wavefunctions, which introduces a variational error. We have focused on clearly quantifying these errors to provide a guide to users of this "standard method" and to guide and prioritize future efforts in this project that will reduce nodal and pseudopotential errors. These systematic studies were made possible by large allocations on DOE supercomputers through the INCITE program and through similar programs at LLNL and SNL.

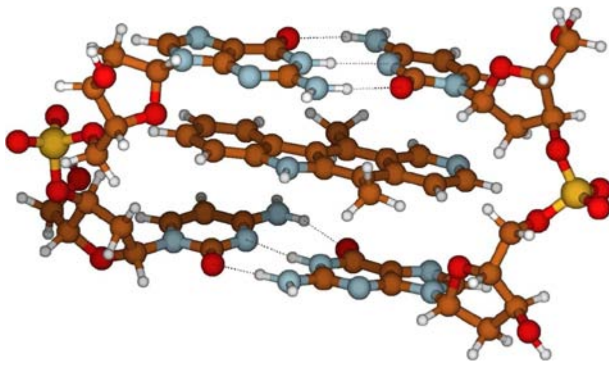

**Figure 1.** Quantum Monte Carlo techniques accurately capture weak van der Waals interactions and can be applied to large systems. From A. Benali et al. (2014), publication [7].

The most accurate, widely utilized QMC method is diffusion Monte Carlo. In 2013 and 2014 we performed a number of benchmark studies aimed at quantifying the remaining errors of this method. This is first time that systematic studies have been performed with careful convergence checks for a broad range of materials in a consistent manner. In [1] QMC calculations were performed for ionic, covalent and van der Waals solids and the optimum lattice constants and bulk moduli obtained. An additional benchmark focusing on van der Waals interactions was also performed [7]. These studies provide a guide to users of the method by providing an indication of the expected error of the method as typically applied, and by providing guidance for equation-of-state type calculations on other materials.

We completed several studies using QMC as a benchmark for assessing cheaper density functional methods, and for selecting more accurate functionals based on the QMC data. Applications include liquid water [4], hydrogen [5], and liquid Krypton [7]. In the latter, a clear improvement of the AM05 functional over LDA is identified for snapshots from a molecular dynamics trajectory, favoring using of AM05 in more extensive molecular dynamics calculations. A study of perovskite and post-perovskite $MgSiO_3$ obtained better agreement with experiment than prior density functional-based calculations [10].

The most significant technical progress is due to the development of the NEXUS workflow software. This software is used to automate the standard process of running a QMC calculation: obtaining a trial set of orbitals from a density functional or quantum chemical code, optimizing a trial wavefunction in variational Monte Carlo, then performing diffusion Monte Carlo for the most accurate result. Traditionally performed “by hand”, this labor intensive and error-prone process has also slowed adoption of QMC. For simple molecular and solid-state systems that fall within a “standard recipe”, running QMC calculations is now extremely simple. The workflow software naturally helps codify working methods for more advanced calculations and also provides a clear provenance for all data. The software and QMC are now accessible enough that we know of at least 1 *undergraduate* student successfully using it for research level calculations, in addition to multiple graduate students, postdocs etc.

NEXUS is currently included with QMCPACK but is suited to automation and workflow tasks beyond QMC. A paper is in preparation.

**Future Plans**

In the next two years we expect to make at least one QMCPACK release every six months. Improvements in QMC methodology based on our scientific goals and experience gained with application to new materials will be incorporated. In terms of technical development, we will incorporate improvements in workflows and automation, including links to additional codes for trial wavefunctions and to different quantum chemical methods. We are currently establishing a formal testing methodology and setting up continuous integration to replace ad hoc testing procedures. Once complete we will publish new documentation and a formal reference paper for QMCPACK. Overall we expect these efforts to establish a firm, modern foundation for the code and to significantly improve its accessibility to new users and other QMC practitioners.

QMCPACK is one of a limited number of materials codes currently able to fully exploit DOE leadership-class computers. Although QMC calculations remain expensive in terms of total CPU hour usage, many calculations can be run quickly by using hundreds of thousands of processors, due to their very high scalability and efficiency. QMCPACK is also able to use current generation GPUs. However, by 2018 a new generation of larger supercomputers will be installed in the US incorporating new architectures. Despite planned participation in the early science programs OLCF and ALCF, we expect to have to invest significant time in adapting QMCPACK to first run at all on these systems, then to run efficiently. We expect that when combined with our planned methodological improvements the range of materials that can be studied to sufficient accuracy with QMC will be significantly increased. For example, systematic studies of transition metal oxides will be possible, enabling materials trends to be uncovered, whereas today only single materials can be investigated.

## Broader impact

We are committed to holding workshops and tutorials to enable new QMC users. Most recently, in July 2014 we organized a training workshop, held at Argonne Leadership Computing Facility, with 33 trainees including 1 from industry. This workshop covered fundamental aspects of QMC through to practical calculations for molecular and solid-state systems using QMCPACK. Every member of the grant was onsite for an entire week to assist with training, lab sessions, and aiding users. Follow-ups are being conducted with the attendees to help apply QMC in their research. All training materials are published online, and professionally recorded & edited recordings of the workshop are published on YouTube. http://goo.gl/3dj3U2

To facilitate usage of the QMCPACK code and implemented methodologies, both for new and experienced QMC practitioners, we are developing substantially improved documentation and tutorials expanded from their workshop form. The same validation tests used by the developers will also be released to users, utilizing the ctest framework, providing vital installation validation and further examples.

## Data Management and Open Access

QMCPACK is fully open source and can be downloaded at http://www.qmcpack.org There are no proprietary or closed source dependencies or components. One of our goals is to improve the accessibility of QMC methods to new users. As part of this effort we have already made several QMCPACK releases. These releases include the entire QMCPACK code itself, plus the full infrastructure and analysis tools necessary for research level calculations. Suggestions for new developments, general queries, and support questions are mediated via a dedicated QMCPACK Google group. The NEXUS workflow tool included with QMCPACK facilitates automation of QMC workflows, and also enables data provenance to be clearly identified. QMC runs traditionally produce little data, leading to simple data management. However we are exploring a new way of storing QMC data, where instead of terse statistical summaries, information from the entirety of the Monte Carlo run is stored on disk/tape. By working with the ADIOS group at ORNL we are able to implement this method at modest additional computational cost [6]. This method enables additional analysis to be performed or new observables measured, even if they were not in the original run (e.g. a more precise measurement of the electronic density, computation of dipole moments, or alternate statistical analyses). These datasets would be made available via the Leadership Computing Facilities, where the data was originally generated.

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# Simulation-Based Design of Functional Sub-nanometer Porous Membranes

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**Keywords:** peptide nanotubes, molecular dynamics, selective transport, nanomechanics, polymer-peptide conjugates.

## Project Scope

The goal of this project is to build a predictive framework to boost the development of molecular separation nanoporous membranes based on self-assembled cyclic peptide nanotubes (CPNs). We use atomistic modeling techniques and theory to derive theoretical guidelines and to identify promising material design rules that guide the experimental efforts while circumventing the synthetic challenges.

## Relevance to MGI

We have maintained constant feedback between experiments, theory, and simulations throughout the project to discuss possible chemistries to tune CP interiors (Fig. 1) and exteriors. For example, early on, experiments suggested that the nanotubes were shortened after conjugating polymer chains to the cyclic peptides. Polymer physics theory and coarse-grained molecular dynamics simulations later guided experiments aimed at using the entropic penalty of polymer chain confinement upon controlling binding energies driving self-assembly. We analyzed the persistence length and mechanical properties of the CPNs, and conformation of conjugated polymers, which lead to joint publications in *Nanotechnology* and *Biomacromolecules*.

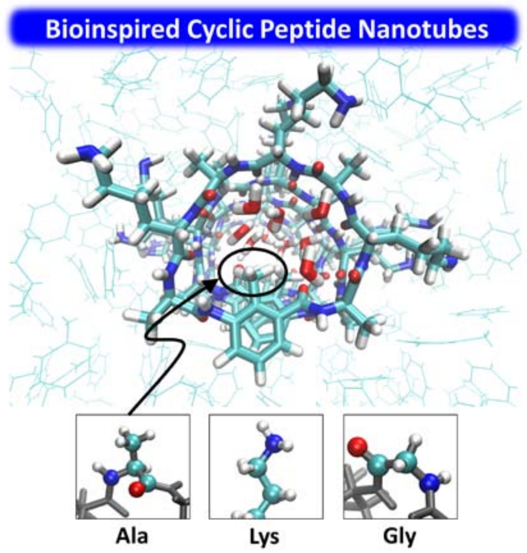

**Figure 1.** Transport through nanopores consisting of cyclic peptide nanotubes with different functional groups. Water flux and selectivity can be tailored by changing interior chemistry, where bulky hydrophobic groups effectively screen ions while still providing high water flux for desalination.

## Technical Progress

Using atomistic molecular dynamics simulations we found that, despite the weak nature of the inter-peptide backbone stabilizing hydrogen bonds, the nanotubes exhibit high Young modulus, 10-20 GPa, similar to other super stiff biological materials such as amyloid fibers or beta sheet crystals found in spider silk (Ruiz et al., Nanotechnology 2013). These results suggest that CPNs are exceptionally stiff despite their small diameter, and hence may serve suitably as rectilinear pores in nanoporous membranes.

We studied the transport of water and ions in chemically functionalized peptide nanotubes (mCPNs). We have identified the role that the interior chemistry of the mutated cyclic peptides plays on the water transport and ion selective properties in bioinspired mCPNs (Ruiz et al., Nanoscale, 2014, **Fig 1**). We are currently exploring nanotubes with heterogeneous chemistries that promise to optimize the flow rate of water while minimizing the transport of ions, of vital importance for water desalination applications.

We studied the growth kinetics and spatial organization of binary mixtures of CPs and found that CPNs exhibit self-similar growth. We found that the striped patterns depend on tempering conditions that control the reversibility mechanisms (Ruiz et al., JPCL, 2014, Fig. 2). We discovered a novel route towards directing the self-assembly of peptide building blocks by polymer conjugation using entropic spring forces (Ruiz et al., Soft Matter 2014).

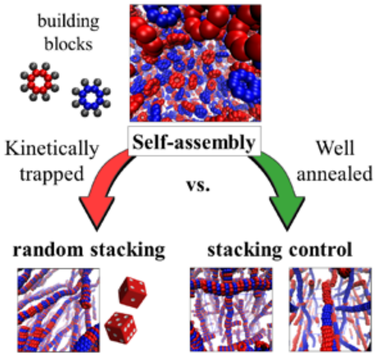

**Figure 2.** Energetic and dynamic factors govern the sequences of CPs in functionalized nanotubes.

### Future Plans

One of our goals is the study of molecular transport in mixed nanotubes of chemically modified cyclic peptides. Another goal is to gain insight into the self-assembly process of polymer conjugated cyclic peptides.

### Broader impact (Optional for DOE grants/FWPs)

This project created undergraduate research opportunities for two women in engineering. Additionally, one REU student and the doctoral student supported by this project established a NanoHUB tool for teaching molecular simulation. The REU student also is a coauthor in one of the published manuscripts.

### Data Management and Open Access

All codes used are open source and simulation results are shared through online repositories where appropriate. For example, we have uploaded our simulation examples on self-assembly of CPNs on NanoHub.

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# Combining Novel Simulation Methods and Nucleation Theory to Uncover the Secrets of Gas Hydrates.

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**Keywords:** hydrates, sampling, phase, coexistence.

## Project Scope

Materials properties are strongly influenced by structural transitions. However, first-order transitions are not easily simulated by conventional methods with temperature as the control variable, due to the instability of the states with coexisting phases. Our generalized replica exchange method (gREM) uses enthalpy as the control variable and converts unstable coexisting states into conveniently-studied stable ones. Methane hydrate formation, and melting/freezing of thermodynamically stable α-ice, and of metastable β-ice with empty cages that hold methane in methane hydrate, have been studied. Success is indicated by a demonstrated capability to find the transition pathways, the structures with coexisting phases, and points on the phase diagrams.

## Relevance to MGI

gREM simulations provide a complete entropic description of phase transitions governing material properties. Results agree with prior simulations and experiment. The surface tension of β-ice against liquid water was determined for the first time. Collaboration with M. Shultz, Tufts Univ., is planned to model her experiments on hydrate inhibitor tetrahydrofuran.

## Technical Progress

Methodology. The gREM ensemble has a temperature function, $T_g(H)$, which determines the sampling weight. We have derived the MD equations of motion that sample an arbitrary generalized ensemble at constant pressure. Using a linear $T_g(H)$ with negative slope the intercept, $\lambda$, controls the single crossing point of $T_g(H)$ with the statistical temperature, $T_S(H)=1/(dS(H)/dH)$, determining the most probable enthalpy; S is the entropy. Thus enthalpy, not temperature, becomes the control variable for the simulation.

First-order phase transitions. We propose a comprehensive approach to systems undergoing first-order phase transitions: (1) MD gREM simulations with multiple replicas, (2) calculation of $T_S$ from replica enthalpy histograms with our ST-WHAM method, (3) entropic analysis and identification of transitions with peaks in $(d\beta(H)/dH)$, $\beta(H)=1/T_S(H)$.

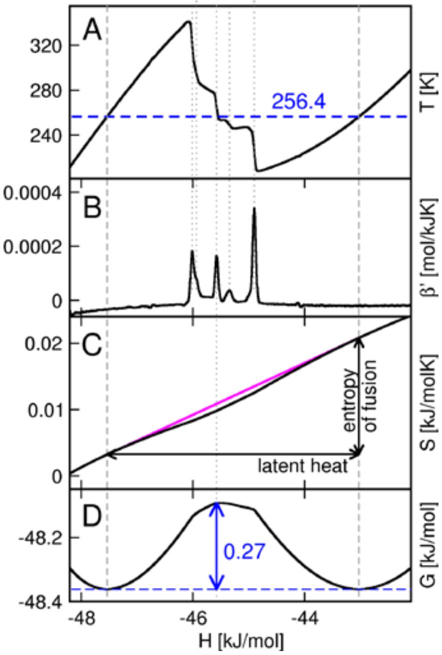

Fig. 1:
Entropic analysis of β-ice melting. **A**, $T_S(H)$; **B**, derivative of $1/T_S(H)$; **C**, entropy; **D**, Gibbs free energy profile at the melting temperature.

β-ice/liquid water transition. The proposed method was applied to the melting of β-ice, under 1 and 200 atm [1]. Figure 1A shows $T_S(H)$. A Maxwell construction on $\beta(H)$ yields the transition temperature as 256.4 K. Peaks in $\beta'(H)$, Figure 1B, indicate locations of subphase transitions between different topologies of coexisting phases, separated by barriers.

Entropy is in black in Figure 1C. The linear Gibbs Hull, magenta, is the entropy of a hypothetical mixture of phases with no surface effects, while the true S(H) function shows the region of positive curvature characterizing first-order transitions. The Gibbs free energy profile at the transition temperature, Figure 1D, has a barrier of 0.27 kJ/mol, giving an estimated surface tension of 26.3 mJ/m^2.

α-ice/liquid water transition. Freezing of pure liquid water to hexagonal α-ice, and melting of α-ice, are strong first order transitions of great interest, and notoriously hard to simulate. The progression of observed structures for melting is: α-ice, ice with a small liquid sphere, a cylinder of liquid in ice, ice and liquid slabs, ice cylinder in liquid, and finally liquid. The transition temperature for ice melting is 269.1 K, correct for the chosen water model. The calculated melting temperature corresponds to a large plateau in $T_S(H)$ where structures consist of liquid and ice slabs [2]. Freezing is governed by a different mechanism and requires cooling to 205 K, the homogeneous nucleation temperature, while melting leads to supercooled water of higher temperature, 223.4 K.

Hydrates. We have simulated formation of methane hydrate starting from dilute solutions of methane in water, under various pressures between 1 and 500 atm, obtaining $T_S(H)$ and identifying coexisting structures using scripts which we have created. The progression is: solution, piece of fully occupied hydrate in water, formation of β-ice around the hydrate in equilibrium with water, and finally conversion of β-ice into α-ice, as expected for a dilute solution. Such observations provide a unique perspective on the mechanism of hydrate formation and the phase diagram.

## Future Plans

We will apply the gREM to hydrate nucleation and growth over a broad range of pressure, temperature and concentration, including the action of inhibitors like methanol and tetrahydrofuran. Our discovery that nucleation occurs from states where $T_S(H)$ is an almost vertical function of enthalpy (middle of Figure 1A) will be used to enhance the usual methods of nucleation theory, e.g. "intervention", to find the critical nucleus.

In attempting to represent bulk systems with coexisting phases in a simulation it is necessary to be mindful of interfacial effects that vanish in the thermodynamic limit. However, in nanosystems the surface effects are properties of the real target system. Thus we aim to exploit the gREM to describe nanosystems with first-order transitions determining material properties relevant to the MGI.

First we will consider hydrate formation in nanopores in rocks, which will include confined water as the zero guest concentration limit. Hydrate growth has been found to be enhanced by clay surfaces and retarded by small pores. Clearly, the effect of the nanoenvironment merits investigation.

The next targets are composite nanomaterials with a metal or biomolecular catalyst core surrounded by a lipid envelope. First-order structural transitions in the lipids, e.g. liquid/gel, control the material properties, switching the catalyst on/off, and enhancing its activity and affinity for the substrate. While lipids have been simulated extensively with standard methods, enhanced sampling of coexisting states of membranes tethered to a core of variable curvature and roughness is new territory. The presence of the core can result in a significant stabilization of the liquid-phase membrane, even for compositions that exhibit gel-like behavior in the bulk. We aim to achieve the capability to predict the properties of an enveloped catalyst, focusing on the control of fluidity by phase transitions as a function of chemical composition, length and density of the lipids, and the core topology. The upshot is computer-aided design of a new class of catalysts, which can be applied to, e.g., hydrogen generation.

## Data Management and Open Access

Our algorithms are implemented into the LAMMPS package, distributed by Sandia National Laboratories, a US Department of Energy laboratory. We have established collaboration with Dr. Chris Knight, Argonne NL, to develop optimized replica exchange and begin supra-million atom simulations on the Mira supercomputer. The MD gREM will be contributed to the LAMMPS distribution for public access.

**Publications**

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# Simulation-Based Predictive Design of All-Organic Phosphorescent Light-Emitting Molecular Materials

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**Keywords:** Purely organic phosphors, TDDFT

### Project Scope

Although prevalent in OLED applications, organometallic compounds exhibit poor stability at short wavelengths, they are costly, and present environmental threats due their rare-earth metal content. Consequently, the purely organic phosphors we recently discovered by serendipity[1–3] provide an attractive alternative. However, despite intensive study, a reliable design principle for purely organic phosphors is still lacking. In this project we therefore combine computational and experimental techniques in a synergistic design cycle for highly emissive room temperature organic phosphorescent materials, establish an integrated design framework, and derive rational molecular design principles for organic molecular electronic materials in general.

### Relevance to MGI

Purely experimental exploration of molecular design requires time consuming development of chemical synthesis routes, while unequivocal separation of multi-varied influences on materials properties is often challenging. Conversely, atomistic simulations can establish the trends in materials behaviors as a function of chemistry, structure, and processing conditions in a fraction of the time. Oftentimes, computational approaches can clearly pinpoint the origin of specific behaviors, allow one to effortlessly change variables that reveal the underlying mechanisms, and thus provide fundamental understanding. In this project computation is used to accelerate discovery by strategically guiding experiments and by identifying targeted materials design principles.

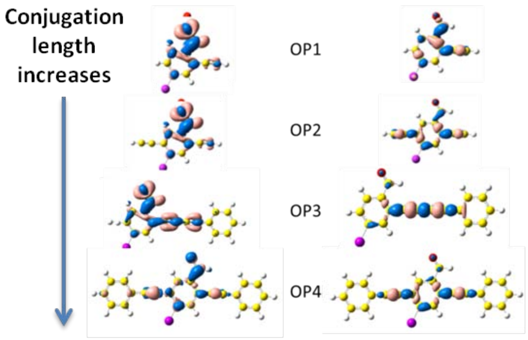

**Figure. 1.** Plot of the total electron density difference between ground state and excited state, isovalue is 0.002 in the unit of electrons/À$^3$, left: $S_0$->$S_1$ , right: $S_0$->$T_1$. The pink represents where loses electrons during the transition, and the blue represents where gains the electrons during the transition.

### Technical Progress

We synthesized a series of purely organic phosphors based on benzaldehyde structures with varied conjugation length and analyzed their photo-physical properties at 77K. The increment in conjugation length results in red-shifted phosphorescence with a lower emission efficiency. Computational investigations of these molecular systems based on time dependent density functional theories (TDDFT) reveals a dramatic decrease in the intersystem crossing (ISC) rates with increasing conjugation length. Calculating the ISC rates between singlet and different triplet excited states we found that the spin-orbit coupling, and thus the ISC rate for $S_1$->$T_1$ is much larger than that for $S_1$->$T_2$. Moreover the $S_1$->$T_1$ ISC rate decreases with increasing conjugation length, which is in perfect agreement with experimental observations. Furthermore, based on the changes in the calculated electron densities of the various molecules when transitioning from the ground state to different excited states, we observe singlet/triplet electron localization.that strongly correlates with the conjugation length. These electron density differences between the ground state ($S_0$) and the excited states ($S_1$ and $T_1$) are shown in Fig. 1. For the $S_0$->$S_1$ transition, large population of electrons is localized around the CHO functional group, whereas the excited electrons are distributed over the conjugated backbone in case of the $S_0$->$T_1$ transition. This implies that triplet states are delocalized, and this is more so the case the farther conjugation extends. As the spatial separation between the singlet and triplet orbitals increases, the spin-orbit coupling efficiency is reduced, which in turn impedes the ISC mechanism. Consequently, expansion of conjugation length results in reduced phosphorescence. We also investigated a series of fluorene derivatives, controlling their electron-donating power via the chemistry of the carbonyl group. Attaching stronger electron donating species to the carbonyl group, shifts the phosphorescence color towards blue, increases the quantum yield, and reduces the phosphorescence lifetime. We achieved phosphorescent quantum yields as high as 49%, simply by embedding the fluorene-based phosphors in an amorphous polymer matrix. First principles calculations to elucidate the relationship between chemistry, molecular structure, and phosphorescent properties of these fluorene derivatives are currently underway.

**Future Plans**

This research aims to further develop this fundamentally new, environmentally benign, and chemically sustainable class of all-organic phosphorescent molecules with improved performance characteristics by employing an integrated computational-experimental approach. With the specific objectives to eliminate the heavy metal ions form the emitting molecules, to lower materials cost and obtainability, improve ease of fabrication, and prolong device lifetime and dependability, our research strategy is to (i) deconvolute the dual roles of halogen bonding, i.e., to promote spin-orbit coupling and suppress vibrational energy dissipation, and supplant the intermolecular secondary bonding-induced phosphorescence enhancement mechanism with intramolecular analogs; (ii) optimize the molecular architectures of both the emitting and host species so as to minimize vibration-mediated non-radiative decay of excited states through stiffening of intramolecular bonding patterns, stabilizing emitters with host molecules designed to suppress detrimental vibrations through effective packing geometries, and crystallizing emitters within nano-confinement; and (iii) understanding and suppressing the detrimental effects of oxidizing environments on device longevity.

**Broader impact (Optional for DOE grants/FWPs)**

The new insights into the functional response of molecular materials gained while perfecting metal-free OLED benefits organic electronics in general, and advance technologies such as photovoltaics, sensors, and displays. Most importantly, we will develop software tools, data management utilities, and workflows for simulation-based predictive materials design approach that can serve as a new paradigm for materials development. The synergy between experimental and computational techniques of investigation will provide students with a broader perspective on modern approaches in scientific research, a rationale that is also implemented in the courses developed and taught by the PIs.

**Data Management and Open Access**

In this project we will generate experimental and simulation based data, as well as simulation code and computational workflows. Data curation will be done following the Open Archives Initiative-Protocol for Metadata Harvesting (OAI-PMH) model used in the National Science Digital Library (NSDL). Accordingly, to each data set or image we attach a header, metadata, and optional containers, all encoded in XML format. To identify the appropriate metadata for a given measurement or simulation outcome, we will develop workflow-driven ontologies that help us to determine the ways in which other users in this field might identify or query data. Our metadata will also contain data provenance. Data will be generated, refined, or condensed at different workflow phases. The workflow typically progresses from (i) raw data (spectra, structures, images) to (ii) data prepared for analysis, to (iii) analyzed data (synthesized information, extracted parameters, model descriptions). The metadata structure for the atomistic simulations includes (i) the mathematical description of the underlying model, (ii) documentation as to the meaning and role of each term, (iii) parameter sets for various materials systems for which the model has been optimized, (iv) references publications on the model, (v) sample code to facilitate implementation, (vi) web logs containing questions and answers concerning user experiences.

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# An Expert Ab Initio Transition-State-Theory-Based Master Equation Code

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**Keywords:** master equation, pressure dependent, transition state theory, ab initio, gas phase kinetics.

## Project Scope

The goal of this project is to develop expert codes for accurately predicting the kinetics of gas phase chemical reactions. The ab initio transition state theory based master equation (AITSTME) approach provides the basic framework for this effort. The code development effort is designed to facilitate all aspects of the implementation of the AITSTME approach while also increasing its utility through further advances in its theoretical underpinnings. A successful code package will be widely used in the modeling of key reactions in combustion chemistry, atmospheric chemistry, astrophysics, and chemical vapor deposition, for example.

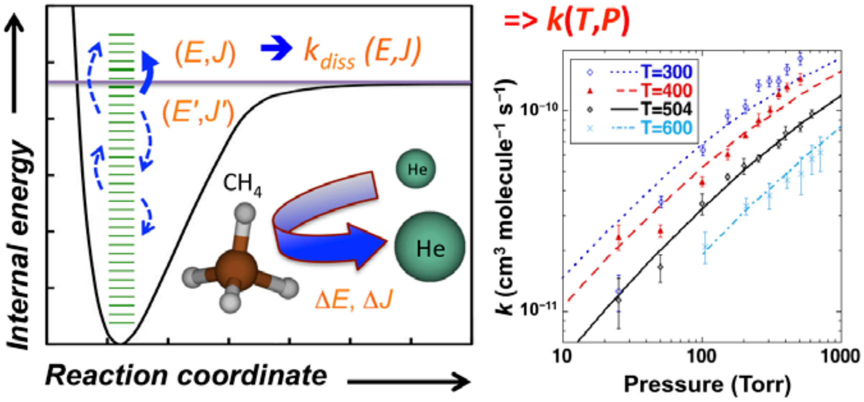

**Figure caption**. "Third-body" collisions activate unimolecular reactants, stabilize energized intermediates, and generally give rise to pressure dependence in chemical kinetics. Here, $CH_4$ + He collisions are shown schematically exchanging energy and angular momentum among the ladder of internal states (*E*,*J*) of methane. Collisions that activate methane above its dissociation threshold promote reaction. The mathematical treatment of these processes yields a priori predictions for the thermal rate coefficients that agree quantitatively with the experimental data.

## Relevance to MGI

The AITSTME approach provides predictions of the temperature and pressure dependence of chemical reaction rate coefficients, which can be used to effectively derive the chemical genome for various gas phase environments. Our recent two-dimensional master equation study of the $CH_4$ and $C_2H_3$ systems aptly illustrates the validation effort for this project (cf. the Figure).[2] Other validations are being performed as part of the Argonne-Sandia Consortium on High Pressure Combustion Chemistry, where the code is currently being used to explore the combustion chemistry genome and the predictions are being compared with a great variety of experimental measurements.

## Technical Progress

Our new general-purpose AITSTME software package, which is termed PAPER (Predictive Automated Phenomenological Elementary Rates), implements a new formulation of the master equation for complex-forming chemical reactions with multiple wells and multiple bimolecular products. The reformulation of the master equation provides compact expressions for the phenomenological rate coefficients describing all chemical processes, i.e., internal isomerization reactions, bimolecular-to-bimolecular reactions, isomer-to-bimolecular reactions, and bimolecular-to-isomer reactions and helps understand the relation between various earlier master equation derivations. The PAPER code, which is now finding widespread use within our team and in external research efforts, incorporates a variety of advances beyond other existing codes. These advances include automated merging of species as their equilibration rates exceed collisional stabilization rates, automatic consideration of all reactions on a given potential energy surface including the generation of PLOG modified Arrhenius fits for all channels, multidimensional quantum and semiclassical treatments of torsions including the variation of secondary vibrations with torsional configuration, anharmonic treatment of umbrella modes, threaded parallelization of the key diagonalization step, a procedure for reducing the matrix dimension through energy dependent species merging, a perturbative procedure that yields more stable results for low temperature, and a procedure for properly modeling the separation into thermal and direct kinetics for hot initial distributions. These advances allow for improved accuracy in the predictions while also greatly reducing the effort involved in making the predictions.

In exploratory work, we have developed a method for making accurate a priori predictions of the pressure dependence of the kinetics.[2] This work required the solution of a two-dimensional master equation (2DME) in energy E and angular momentum J, as well as accurate calculations of collision induced E and J transfer rates. These calculations were accomplished with codes developed as part of this project. Specifically, new methods for characterizing details of the collisional transfer function that are not typically considered (J-dependence, E/J coupling, etc.) were developed and implemented in the molecular dynamics code DiNT, while a new two-dimensional master equation code was developed. Furthermore, our universal $C_xH_y$ + M potential energy surface (PES) methods (designed specifically for accurate and efficient collisional energy transfer calculations) were separately extended to include M = $O_2$ and were validated for larger unimolecular targets.

In other work, DiNT was further improved with a new method for predicting spin-forbidden kinetics and with options for computing exact classical diffusion coefficients. Several strategies for obtaining Lennard-Jones parameters (for use as collision rate parameters in elementary kinetics calculations and as transport parameters in detailed chemical kinetic models) were developed and compared with exact classical results. A particularly useful approximation was interfaced with our universal PESs and incorporated into a stand-alone code called OneDMin.

## Future Plans

Continued progress in the automation of the kinetic predictions will require further consideration of the coupling to ab initio electronic structure evaluations. Direct coupling with the KinBot program, which is being developed under separate DOE-BES support, will facilitate the generation of the key stationary point properties for the PES. Additional work on automatically producing quantitatively accurate PESs for dynamical calculations of quantities such as energy transfer functions, nonadiabatic transition rates, and roaming-radical fractions is planned. Further work on more general programming of the 2DME is also planned. A final topic of interest involves the development of coupled master equations that treat a succession of reactions without the presumption of thermalization at each stage of the reaction.

## Data Management and Open Access

We have distributed our AITSTME master equation code (PAPER) to select users (~20 groups thus far) for the purposes of beta-testing. A web release of the code is planned for the near future. Two other codes developed as part of this work are freely available online:

**DiNT:** Direct Nonadiabatic Trajectories. A molecular dynamics program for adiabatic and nonadiabatic chemistry, version 1.1; A. W. Jasper, C. M. Oana, and D. G. Truhlar, Sandia National Laboratories and University of Minnesota (2013). http://sandia.gov/~ajasper/dint

**OneDMin:** One-Dimensional Minimizations. A code for calculating Lennard-Jones parameters from detailed intermolecular potentials; A. W. Jasper and J. A. Miller, Sandia National Laboratories (2013). http://sandia.gov/~ajasper/onedmin

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# Coupling Electrons, Phonons, and Photons for Nonequilibrium Transport Simulation

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**Keywords:** multiphysics, quantum transport, nonequilibrium, nanostructure, time-dependent

## Project Scope

The objective of this project is to develop versatile computational tools for accurate simulation of the far-from-equilibrium and time-dependent quantum transport in realistic semiconductor nanostructures driven by high-intensity dc or ac electromagnetic fields. The key challenge in simulating nonequilibrium time-dependent transport is that one must capture the strong coupling between electrons, phonons, and electromagnetic fields in the same simulation, self-consistently and at every time step.

## Relevance to MGI

This project relates closely to experimental measurements of electronic, thermal, and optical properties of a variety of semiconductor nanostructures. For example, we predicted that uniformly doped double-barrier tunneling structures would act as emitters of THz-frequency radiation [1]; these are being fabricated by the PI's collaborators. The inclusion of nonequilibrium phonons affects measured performance of quantum cascade lasers (QCLs) in significant ways, leading to much better agreement between theory and experiment in the temperature performance [2]. Considering that QCLs are the highest-power coherent light sources at midinfrared and THz frequencies, this work significantly advances our understanding of the coupling between electrons and phonons in QCLs, aiding their widespread applications (Fig. 1).

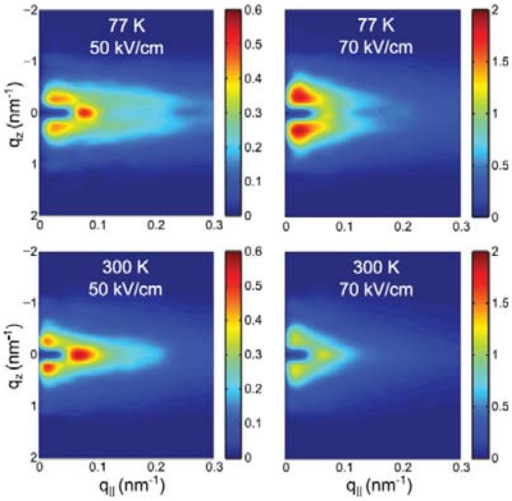

**Figure 1.** Nonequilibrium phonon occupation number (red – high, blue – low) at different fields and temperatures versus in-plane and cross-plane momentum in a GaAs-based midinfrared quantum cascade laser. The excess phonons exist only near the Brillouin zone center, but their population is drastically higher than in equilibrium. They strongly affect electronic transport, largely by amplifying electron scattering with phonon absorption. From Shi and Knezevic [2].

## Technical Progress

With high-intensity fields, considerable energy is pumped into the electron and hole systems, which relax by transferring much of it to the lattice; thereby, both electronic and lattice (phonon) systems are far from equilibrium. With high-frequency excitation, both interband and intraband electronic transitions potentially occur, and details of the interaction between the the electronic systems and the fields are critical to capture. Three main directions have been undertaken during the course of this project (currently 2 years and 4 months in): a) high-frequency or time-dependent transport in nanostructures [1,3,4], b) nonequilibrium phonons in quantum cascade lasers (good example system for high-field dc transport) [2], and c) phonon transport in realistic confined structures of experimentally relevant sizes [5]. Under a), we calculated the ac conductivity, dielectric function and plasmon dispersion of graphene, with focus on the role of substrate impurities [3]. We also showed that self-sustained THz-frequency current oscillations occur in uniformly doped double-barrier tunneling structures, a phenomenon well documented at much lower frequencies in superlattices [1]. Under direction b), we demonstrated how critical it is to account for the coupled dynamics of electrons and phonons in far-from-equilibrium systems, especially at low temperatures. We have for the first time fully quantified the influence of nonequilibrium phonons on QCL operation (Fig. 1). Under c), we have developed a full-dispersion phonon Monte Carlo algorithms for 2D systems with hexagonal symmetry, like graphene nanoribbons, and elucidated the universal phonon transport features in nanowires with rough correlated surfaces (Fig. 2).

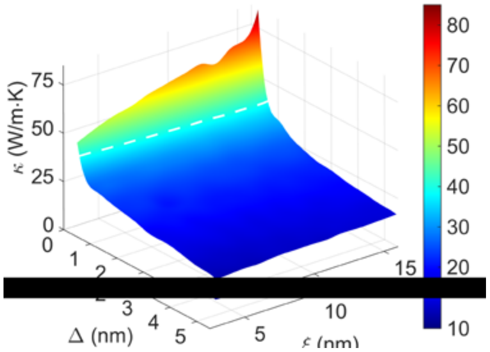

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**Figure 2**. Thermal conductivity κ in 70-nm-wide Si nanowires with exponentially correlated real-space surface roughness of correlation length ξ and rms roughness Δ. The dashed line denotes the Casimir limit, the lower limit on thermal conductivity that is obtainable with the specularity model for phonon interaction with the boundaries. With real-space roughness, it is clear that a vast parameter space results in thermal conductivity below the Casimir limit, as seen in experiment. From Maurer *et al.* [5].

## Future Plans

The work under a) and b) will merge as we include coherent tunneling effects with Wigner Monte Carlo along with nonequilibrium phonon effects for unprecedented accuracy in the modeling of heterostructures and superlattices far from equilibrium (Fig. 3). We will extend the effort to systems with 2D transport and look at how highly delocalized carriers, such as electrons in quantum point contacts at low temperatures, couple with light and how they respond to time-varying biasing. We will complete the work on the dielectric function and plasmons in graphene nanoribbons and look into ways to "numerically" excite plasmons in graphene-based nanostructures with very accurate electronic and dielectric properties. Emergent related work is on diffusion of excitons through carbon nanotube composites.

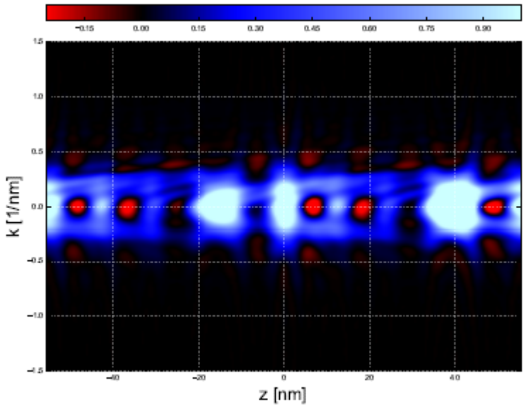

**Figure 3.** (*Preliminary data*) Wigner function (represented by color) versus position and wave vector for a THz quantum cascade laser. Red denotes thenegative values of the Wigner function, which indicates coherent transport (tunneling). This type of simulation is computationally only marginally more intensive than semiclassical Monte Carlo, but capture coherent transport very well. Jonasson and Knezevic, in prep.

## Data Management and Open Access

Raw data, source code, and figures are being stored for a minimum of three years past the end of either this award or publication, whichever is later. The codes will be made publically accessible (GPL-v3) within the next several years.

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# Adaptive fine-scale structure design: from theory to fabrication

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**Keywords:** fine-scale structures, homogenization, shape optimization, additive fabrication

### Project Scope

This project is exploring the use of 3D printing to make structured artificial materials with advantageous physical properties. More specifically, the project is developing methods for adapting the fine-scale structure of a manufactured object to its macroscopic shape and function. While 3D printing processes have restrictions that present challenges (e.g. the need for support material or self-supporting structures, and limitations on resolution), these processes offer unparalleled flexibility in the choice of structure, making it feasible to explore a large space of possibilities both computationally and experimentally.

**Figure.** Left: a cell of a negative Poisson ratio (-0.4) periodic structure. Right: highly isotropic low Young modulus structure satisfying manufacturability constraints.

### Relevance to MGI

This project is integrating theory, computation and experimental measurements. In current work, the formulations we are using are based in part on previous theoretical developments of shape optimization by homogenization. Extensive computation-based searches are used to discover periodic structures approximating target homogenized elastic properties. Sample patterns are produced using stereolithography-based printing (in the future, we will also use a specialized printer using biomaterials). Already at this stage, fabrication informs theory and computation, as not all patterns end up being manufacturable. Elastic properties are measured and compared against those predicted computationally, and the results are used to inform further computational exploration.

### Technical Progress

This project started in September 2014, building on an initial foundation of previous unfunded work done in Spring 2014. Progress has already been made in several directions:

1. A large space of truss-like periodic structures with cubic symmetry has been explored computationally, with the goal of identifying manufacturable structures with a high degree of isotropy that cover a maximal part of the set of possible Hooke's laws (e.g. Young's moduli and Poisson ratios).
2. We are developing software for the evaluation and optimization of homogenized properties of truss-like structures, as well as software for optimizing the spatial variation of (homogenized) material properties, for use as part of the shape-optimization pipeline.
3. Manufacturability criteria are being developed for a stereolithographic printing process, quantifying the minimal allowable feature size, distance between features, connectivity, and maximum overhang size.

4. We have conducted a series of tests of some initial patterns, testing the pipeline from the initial pattern optimization to measurement of properties. This has led to initial conclusions about systematic corrections required for a better match between predicted and measured properties.

**Future Plans**

This investigation will draw on recent mathematical advances concerning the effective properties of heterogeneous media; it will draw on recent computational advances concerning the representation, design, and simulation of geometrically complex structures; and it will draw on recent advances in biomechanics, where the design and manufacture of bone scaffolds has been a major driver of research activity. The challenges associated with 3D printing will drive further development in all these areas. For example: (1) past work on structural optimization has mainly considered linear models of material response, whereas plasticity, brittle failure, and buckling may be important for structures made by 3D printing; (2) past work on optimal microstructures has focused mainly on mechanical or physical properties such as the effective Hooke's law; for some applications, non-mechanical characteristics such as porosity are also very important; (3) past work on structural optimization has suggested that hierarchical structures such as "sequential laminates" may be useful, but they were previously considered unmanufacturable; with 3D printing, the manufacture of such hierarchical structures seems within reach. Most of the project's budget is for the support of students and postdoctoral researchers, who will gain a unique interdisciplinary experience through their involvement in the multidisciplinary effort.

**Broader impact**

Two Computer Science PhD students are already involved in the project. We are currently reviewing candidates for a postdoctoral position funded by the award. In years 2 and 3, masters students in the department of Biomaterials at the dental school will join our activity. We expect each junior participant to engage in more than one aspect of the project. For example, one of the Computer Science PhD students has already acquired a significant experience in experimental measurements, under the guidance of the dental school co-PIs. Another example: a stereolithography 3D printer purchased with the award (marketed as B9Creator) has an open hardware and software architecture, and is maintained by the students involved in the project.

**Data Management and Open Access**

We expect that the main outcome of the project will be a collection of methods for generating fine-scale structures with desired parameters; we are already collecting some initial datasets (generated using NYU’s HPC facilities) as well as measurements of fabricated sample patterns. The data are stored on the Courant Institute’s servers with an off-site back up system and are at this time available to project participants. In addition to publications describing the methodology we develop, we expect to make CAD files describing useful patterns available online, accompanied by associated experimental measurement data. We also will work towards releasing a part of the experimental software we are developing.

**Publications**

Does not apply – the project just started in September 2014.

# DNA-Grafted Building Blocks Designed to Self-Assemble into Desired Nanostructures

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**Keywords:** DNA grafted nanoparticles, Supramolecular Assembly, Reverse Design, Optimization.

## Project Scope

We develop transformative, computer-based tools to design DNA-grafted colloids (DBB) that will spontaneously assemble into desired crystal structures. Our proposed "Product Design" mode of research (Figure) runs counter to the Edisonian approach where building blocks are first synthesized, and then examined as to the structures they assemble into. A primary feature of our approach is that we develop hybrid genetic algorithm based methods to replace this trial-and-error methodology with one that can design DBB that will assemble into desired structures. While our model predictions are critically validated against experiments, the more important point is that this new methodology can revolutionize materials design.

## Relevance to MGI

Our team has complementary experimental and theoretical skills crucial to its success. Venkatasubramanian and Collins are expert in the mathematical optimization and machine learning tools that are essential for successfully implementing the "Product Design" concepts. Kumar is expert in Monte Carlo/Molecular Dynamics algorithms for simulating colloidal assembly. Gang, is a pioneer in experimentally assembling DNA-grafted colloids, and in characterizing these assemblies. Kumar, Gang, and Venkatasubramanian have collaborated on designing DNA-grafted nanoparticles that assemble into ordered arrays. Four papers (one appeared in PNAS, one each in review in PNAS, in JACS and in Nature) point to the essential collaboration between experiment and theory.

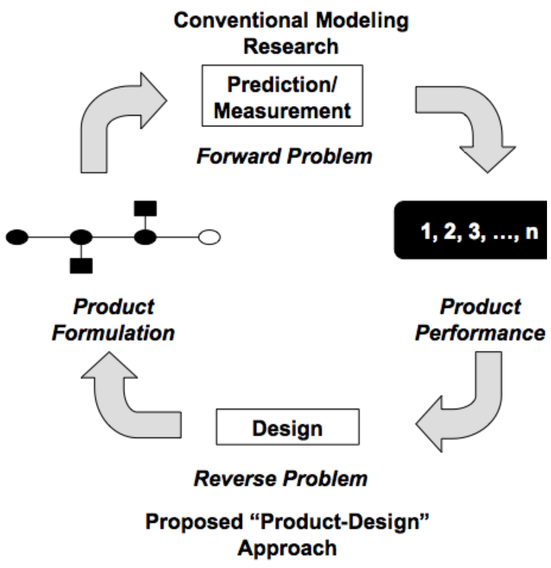

**Figure.** Comparison of conventional and proposed paradigms

## Technical Progress

Our first paper, published in PNAS, focused on the development of the design methodology that is the central focus of the proposal. To date, experimentally it has been found that DNA grafted colloids formed four different structures – CsCl, $AlB_2$, $Cr_3Si$ and $Cs_6C_{60}$. This must be viewed in light of the crystal database which suggests that several hundred known crystal structures exist. Our paper has focused on finding regions of parameter space where these other structures may be found, and made several predictions for new structures – for example we suggested that structures such as $Cu_5Zn_8$ and $Pd_5Th_3$, among others, could be formed. Experimental verification of these results raised the important question of what the stoichiometry needs to be to observe these structures. That is, do we need to mix colloids in the ratio 5:8 to observe the $Cu_5Zn_8$ structure, or is the result robust to the chosen stoichiometry. While there are important exceptions, a generally accepted view is that the right stoichiometry of the two building block colloids need to be mixed to form the desired crystal structure. In a paper under review in PNAS, we combine experiments and theory on a series of DNA-grafted nanoparticles at varying stoichiometries, including non-integer values, to probe this open question. Both experimental results and theoretical calculations reveal stoichiometry as a new parameter that can couple with the geometries of the building blocks to tune the equilibrium lattice. Theory also shows that phase coexistence between crystal polymorphs can sometimes occur in regions of non-integer stoichiometry. Thus, while stoichiometry can be a powerful handle for direct control of lattice formation, care must be taken in its design and selection to avoid polymorph coexistence. Another variable we have studied in a paper under review in Nature is to use osmotic pressure, specifically through the addition of PEO to the solution, to facilitate crystal morphology transitions. The theory for this result remains to be developed.

## Future Plans

The unfortunate issue that these works have raised is that it appears the spherical DNA grafted colloids only appear to assemble into CsCl, $AlB_2$, $Cr_3Si$ and $Cs_6C_{60}$. Obtaining other structures probably requires us to go away from spherical building blocks, and we have recently begun to develop new modeling tools to handle these more complicated shapes. The further development of these modeling tools, the affiliated machine learning tools and validating experiments then represent the focus of research over the next year.

## Broader impact (Optional for DOE grants/FWPs)

Controlling the directed self-assembly of DNA-grafted nanoparticles (DNA-NP) into superlattices with well-defined crystal morphologies have consequences for photonic and plasmonic properties with applications in spectroscopy, surface imaging, and optical sensors. Further, they are also relevant as catalytic nanostructures, nanomachines, and biological delivery vehicles. From a human viewpoint, our work has trained a post-doc (Babji Srinivasan) who is a faculty member at IIT Gandhinagar (India). A second student, Thi Vo, is in his third year and making rapid progress. Two new students (Akansha Singh and Sudhikha Sridhar) have just begun to work on this project.

## Data Management and Open Access

The data produced in the course of the project will be both simulation based and experimental. A large volume of raw data generated will include simulation-derived trajectories. The computer cluster owned by the PI provides space for data and code storage. Access to the data/code will be made available to the public upon request. The data/code will be made available to the public after the results are accepted for publication. To gain access to the data, the person will need to contact the PI directly. There is no privacy or intellectual property issues associated with the data/code generated in this project. No permission restrictions will be placed on the data/code.

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3. "Selective Transformations of Nanoparticle Superlattices via DNA Interaction Re-Programming" Zhang, Y., Pal, S., Kumar S.K., Gang, O. *Submitted to Nature.*
4. “Dynamic Tuning of DNA-Nanoparticle Superlattices by Molecular Intercalation of Double Helix” Zhang, Y., Pal, S., Kumar S.K., Gang, O. *JACS in review.*

# Engineering Strength and Toughness into Metals

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**Keywords:** Twin mesh engineering, twin-twin interaction; strength, toughness, HCP metals

### Project Scope

The DMREF program, between University of California at Davis (UCD), Georgia Institute of Technology (Georgia Tech) and Los Alamos National Laboratory (LANL), responds to the challenge of accelerating materials discovery and implementation by constructing a fundamental knowledge base to design materials from basic principles that have specific combinations of strength and toughness. A synergistic experimental-modeling approach is implemented to strengthening and toughening in HCP metals via the concept of "twin mesh engineering". Hypothesis is that twin meshes, two or more intersecting arrays of twins within a grain, can be engineered to attain unprecedented combinations of strength and toughness in HCP metals.

### Relevance to MGI

The DMREF program is to promote materials discovery and design with close, iterative feedback loop between materials processing, properties, and modeling. The approach will be applicable to HCP metals that commonly deform by slip and deformation twinning. Ex-situ and in-situ mechanical deformation experiments on Mg and Zr will be carried out systematically to explore the orientation dependence of twin mesh formation and expansion. The analyses will be directed with a view towards advancing the atomistic and polycrystalline plasticity models. These models will be to predict the textures and deformation processes needed to create microstructures profuse with twin meshes. For validation, bulk processing and characterization on polycrystalline Mg and Zr will also be performed. Finally, constitutive model predictions and mechanical test results for strength and toughness will be compared and linked back to the twinned-mesh microstructure. We will iterate on these steps in order to achieve basic understanding and predictive capability of processing-microstructure-property loop.

### Technical Progress

We have initiated research aimed at understanding twinning and twin-twin interactions in deformed Mg single crystals by EBSD and TEM. Preliminary results suggest that multiple nucleation of different twin variants could indeed divide the matrix into sub-structures. Figure 1 shows multiple twin nucleation and twin-twin interactions in a deformed single crystal Mg sample. One can hypothesize that the existing fine-structured twins can impede the propagation of new twins, which further helps maintain the overall fine sub-structures. We have already started advancing our HCP single and polycrystalline modeling tools to account for multiple twin variants and twin types within individual crystals. Moreover, an in-situ TEM study is being pursued at National Center for Electron Microscopy (NCEM) at Lawrence Berkeley National Laboratory, in order to: (1) capture the initiation of twinning events; (2) study the dislocation structure in the vicinity of embryonic twins; (3) therefore understand the nucleation mechanisms of twinning and the possible interactions between slip and twinning.

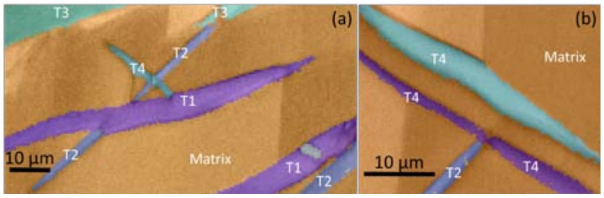

**Figure 1**: Multiple twin nucleation and twin-twin interactions in a deformed single crystal Mg sample. Lenticular-shaped areas are all {10-12} type "tension" twin, and different colors stands for different variants of {10-12} twin [unpublished work].

### Future Plans

This DMREF program will tightly integrate experimental and modeling efforts across UCD, Georgia Tech and LANL. To engineer twin meshes, existing theoretical models will be used to guide *in-situ* experiments and in turn, experimental results will be used to formulate and/or refine physical models that can ultimately be used to increase the accuracy of model predictions. Current and updated versions of the computational code and experimental data will be exchanged across the three institutions. With this integrated experimental-modeling program, the research efforts are being dedicated to explore and answer the following three fundamental questions for HCP metals. First, is slip an essential precursor to twinning and if so, how does it influence twin nucleation and thickening? Second, how are twin/slip and twin/twin interactions accomplished? Third, what texture and deformation conditions are needed to produce a high density of twin meshes? The mechanistic information derived from transmission and scanning electron microscopy in-situ deformation experiments will be used to refine existing physical models, and formulate novel ones as new mechanisms are discovered. In-situ deformation experiments using single crystals of Mg and Zr will be conducted to systematically explore the orientation dependence of twin mesh formation and thickening. From these results, the models will be upgraded and the textures and deformation processes needed to create microstructures profuse with twin meshes will be predicted. Bulk processing and characterization on polycrystals of these two metals will also be carried out to validate these predictions. The selection of these two metal systems, Mg and Zr, is based on the fact that Mg deforms primarily by basal slip and Zr primarily by prismatic slip. Hence these systems will allow us to systematically study the influence of different slip planes on the physics of twin mesh formation and thickening.

### Broader impact (Optional for DOE grants/FWPs)

The **broader impact of the DMREF program** is a solution to the long-standing problem of strengthening and toughening in HCP metals via an ingenious notion of ***"twin mesh engineering"***. The research formulates the scientific framework required to design twin meshes that can be used to attain unprecedented combinations of strength and toughness in HCP metals. This approach has a generic application to materials that deform by twinning. The DMREF program facilitates complementary collaborations and academic exchanges through mutual visits, in particular with participation of students at graduate level between LANL, Georgia Tech and UCD. For instance, one UCD graduate student supported by this DMREF program is already planning the first of many extended visits to LANL for model development.

This DMREF program is instrumental in attracting young engineering undergraduate students, and expose them to state-of-the-art interdisciplinary materials research. The program encourages the involvement of undergraduate students from underrepresented groups, thus providing them with learning opportunities to science, technology and engineering subjects in a research context. The research activities are to provide excellent educational experiences for the graduate students involved. Students are encouraged to present their research at national and international meetings. Relevant interdisciplinary research activities can provide the students an in-depth understanding of scientific phenomena in materials science and engineering. Outreach is to be made to regional universities and colleges, which builds upon existing infrastructures and working relationships with those institutions. Representatives for the DMREF program is also to initiate outreach at the K-12 level.

### Data Management and Open Access

The Data Management Plan (DMP) is to be created and maintained to: (1) ensure the preservation of the data collected through the DMREF program, as well as any results derived from associated research; (2) provide the appropriate protection of intellectual property generated from the DMREF program; and (3) implement the dissemination and sharing of the associated research results created from the DMREF program. This DMP covers the data to be generated and collected through the collaborative research for the DMREF program at the UCD, Georgia Tech and LANL. The majority of information generated will be stored and archived through both publication in the research literature and on a website. With each file there will be a pdf document describing the source, the data acquired and the data format. Access to the archived data will be granted for noncommercial research-based individuals or groups. Data archived after acquisition will become available for others after the team has validated and analyzed the data. For commercial use of the information, inquiries will be directed to the UCD Innovation Access team who will assist in complying with all UC, State and Federal guidelines.

### Publications

D.L. Zhang, H.M. Wen, Y.Y Wang, B. Saller, F. Chen, L.M. Zhang, M. Li, I.J. Beyerlein, J.M. Schoenung, S. Mahajan, and E.J. Lavernia, *Tension/Compression Yield "Symmetry" and Reduced Strength Differential in Mg-Y alloy*, Acta Materialia, submitted (December, 2014).

# Designing Tunable Au-Based Bimetallic Nanocatalysts

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**Keywords:** bimetallic catalysts, site-directed synthesis, structure-function catalysis.

## Project Scope

The increasing demand for more optimal catalysts requires more efficient and selective catalysts that are less harmful and relatively inexpensive. Gold-based bimetallic nanocatalysts provide greater tunability in nanostructures and chemical compositions than their monometallic counterparts due to undeniable advantages resulting from the alloying "synergy" of gold and a second metal. With recent advances in nanoscience and nanotechnology, it is becoming easier to synthesize, manipulate, and characterize tunable Au-based bimetallic nanocatalysts.[1,2] We will computationally design and subsequently synthesize tunable catalysts to improve the reactivity, selectivity, and stability; thereby increasing catalytic efficiencies.

## Relevance to MGI

On the basis of strong scientific and application-driven interests in bimetallic nanocatalysts, we propose to computationally design $Au_nAg_m$ and $Au_nCu_m$ bimetallic nanocatalysts and expand our first principles knowledge to other Au-based catalysts. Ultimately, our goal is to build a detailed structure-function mapping of Au-based bimetallic nanocatalysts. *We will develop a set of high-throughput algorithms that will create structure-property maps which will further enable the design of nanocatalysts for energy and environmental applications.* The impetus for this project lies in the need to develop schemes that build on the multitude of material properties, accurately predicted and measured at the nanoscale, for designing functional materials with tailored properties at the mesoscopic scale.

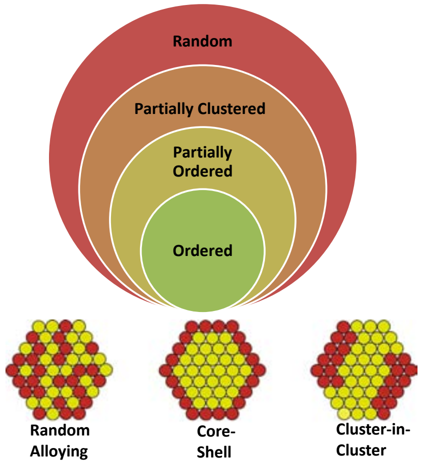

**Figure.** Starting from highly ordered building blocks we build a structure-function database of the reactive properties of these building blocks. Building blocks can then be extended to understand the properties of larger nanoparticle systems which will guide synthesis of site-directed bimetallic catalysts.

## Technical Progress

The proposed research will comprehensively advance both technical and conceptual understanding of the structure-function mapping in bimetallic catalysts. We will build a guidance framework to design and develop bimetallic catalysts from first principles rather than trial-and-error by decreasing the number of potential nanoparticles to an experimentally manageable number. We will produce transformative algorithms and the developed methodologies are knowledge gained by the scientific community as we release software and algorithms to the scientific community for general use.

## Future Plans

While our chosen prototype is Au-based bimetallic nanoparticles, the framework to be obtained can be more generally applicable for predictive modeling of functional nanomaterials. We will utilize high-throughput calculations of reactive properties to guide and refine a research framework "*aimed at understanding fundamental* *chemical structure and reactivity and fundamental intermolecular interactions that underpin and will enable the future discovery and design of new materials with predetermined properties and multifunctional capabilities."* There are several key properties of these nanoparticles: the size, shape, composition, and stoichiometry. To begin with the genetic algorithms will proceed in two stages: "stoichiometry evolution" for a series of nanoparticles of fixed sizes and the second of an "overall evolution" (which combines size and stoichiometry). The size and shapes of these building blocks will be determined both by what is experimentally feasible and what is predicted to be optimal *vis-à-vis* the desired functionality, the chemical reactivity of Au-based bimetallic nanoparticles.

Since stability is of prime concern, we will examine the structural, vibrational and thermodynamic properties of the nanoparticles. Theoretically and computationally, this would entail paying full attention to the geometric and electronic structure and their evolution with temperature. We will utilize data from synthesized and characterized structures as feedback elements in our nanoparticle design. The projects will consist of the following thrusts:

- Computational modeling of chemical characteristic of small (< 2 nm) Au-based bimetallic nanoparticles
- Development of new genetic algorithms for nanoparticle geometric structure optimization
- Synthesis and characterization of Au-based bimetallic nanoparticles
- High throughput modeling of larger (> 2 nm) Au-based bimetallic nanoparticles (investigating different size, shape, composition, and stoichiometry)
- Au-based bimetallic nanoparticles (small & large) properties for structure-property database.

## Broader impact

Our proposed research will benefit energy technology that is currently being pursued by experienced researchers at the National Energy Technology Laboratory and this collaboration will continue to promote regional collaboration regarding catalyst design in energy applications. The proposed research will boost the current interdisciplinary collaborations along existing established pathways and thus will impact regional outreach and educational impact for students. The PIs will continue to engage under-represented student populations in their research programs and they will continue to cultivate broadened participation for their professional preparations. The National Energy Technology Laboratory is engaged with industrial partners and the research knowledge gained and catalysts designed will extend to these industrial partners.

## Data Management and Open Access

Currently, our electronic-structure software package FIREBALL with molecular-dynamics capabilities is freely distributed.[3,4] By first quarter 2015, we will port a newly developed energy-only and Fukui-function evaluator (using the core components of our FIREBALL code) to Sourceforge, or another popular online software sharing resource sites for use by interested third parties. We are currently in the final development stages of a new, more user-friendly, stream-lined FIREBALL code. Therefore, in later stages, as the project progresses, we will port a newly "stable" source of all software components of our FIREBALL software to Sourceforge (or another third party sharing resource).

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# Machine learning for many-body physics

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**Keywords:** Machine learning, strong correlations

## Project Scope

Our problem concerns the application of machine learning (ML) to many-body physics. It is in its infancy, and we are the first team to apply it to strongly correlated electrons. Our final aim is to use ML as a substitute for numerically intensive calculations in dynamical mean-field theory (DMFT), one of the most important numerical method available for non-perturbative systems. Using both classification (metal-insulator) and regression, we want to reconstruct DMFT for model Hamiltonians as well as for real materials calculations.

## Relevance to MGI

Many interesting materials have strong enough electronic correlations that standard electronic structure methods cannot be used to describe them. Simplified treatment of the local correlations using DMFT offer "good enough" predictive capability for many materials but the methods are too computationally intensive to be applied to wide surveys, and the transferability of parameters in effective Hamiltonians is not understood. We are focusing on transition metal oxides, where we can compare results on ordered and disordered alloy series with samples grown by oxide MBE.

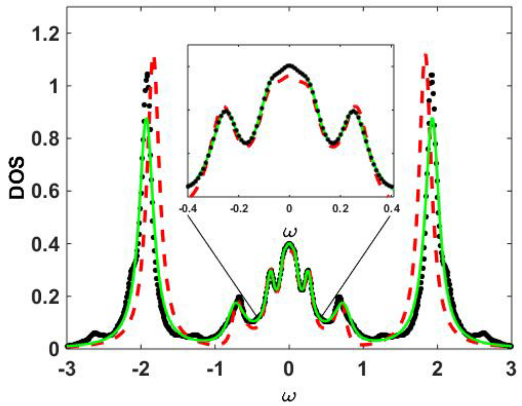

**Figure 1. Machine learning prediction for the density of states using the Legendre polynomial representation for half-filled AIM with *U = 3.04.* Dots (.) denote the exact result, red dashed lines (--) denote the result for a learning set of length 500, and green lines (-) denote the result for a learning set of length 4999. See [1] for details.**

## Technical Progress

We showed that ML can be used efficiently for the Anderson impurity model (AIM) [1]. Different methods of parametrizing the Green's function were investigated such as learning directly a function in imaginary time or imaginary frequency, and a representation in terms of Legendre polynomials was found to be superior due to its limited number of coefficients and its applicability to state of the art methods of solution (see Fig.1). We are now finishing to show its use as a solver for dynamical mean-field theory in the case of model Hamiltonians. ML for many-body physics in the case of AIM and DMFT can be presented as a way to predict the relation between two functions: the hybridization function and the interacting Green's function. In DMFT applications a key issue is the choice of descriptor, the data representation used as input for ML, which is not dependent on the impurity solver. Different parametrizations are being examined. The ability to distinguish metallic and Mott insulating solutions is also analyzed. We are also finishing exploring backward ML at model Hamiltonians level, in which a desired density of states (DOS) is used as input for ML, and the physical system that would be needed for such a DOS can be predicted. This is reverse engineering using ML for predicting structures for desired properties.

## Future Plans

Real materials calculations are computationally very intensive and therefore, in the long term, one of the ultimate goals of ML in many-body physics is its application to real materials situations. Of great interest would be the idea of reverse engineering that was mentioned for model Hamiltonians above. This would enable us to infer desired heterostructures and materials from desired properties. This is a long-term project and will involve constructing large datasets of solved problems. This calls for an international collaboration where groups from all over the world could deposit in a public database their solutions once they are done with their problems of interest. This could be maintained as a website shared among members of the collaboration.

## Data Management and Open Access

Our plan to maintain a website to enable others to deposit their data would also make accessible the codes used to train and predict our machine learning scheme which would in effect give contributors the possibility to also predict their own structures.

## Publications

1. Louis-François Arsenault, Alejandro Lopez-Bezanilla, O. Anatole von Lilienfeld and Andrew J. Millis, Machine learning for many-body physics: The case of the Anderson impurity model, Phys. Rev. B, **90**, 155136 (2014)

# Center for Gas Separations
# Relevant to Clean Energy Technologies

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**Keywords:** carbon capture; materials and chemistry by design; nanoscale science; solid sorbents; membranes

### Project Scope

The mission of the Center for Gas Separation (CGS) is to develop the fundamental science necessary for tailor-making materials and membranes for the efficient separation of gas mixtures, particularly as required in the clean use of fossil fuels and in the generation of alternative fuels.

### Relevance to MGI

The new metal-organic frameworks synthesized within the CGS provide lead compounds exhibiting important new gas separation properties that can then be taken into the MGI. The MGI could potentially then identify additional materials exhibiting similar or even enhanced properties for that particular gas separation. Ultimately, this iterative process and relationship can be expected to reduce the substantial energy costs associated with gas separations.

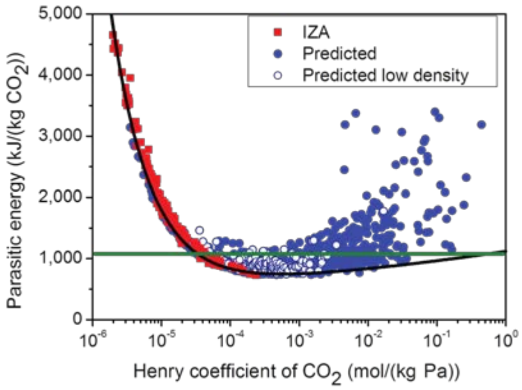

**Figure.** A computational approach was developed to screen millions of sorbents for their carbon capture performance, as measured by the parasitic energy [15].

### Technical Progress

The focus of the CGS is to develop novel materials for energy-efficient gas separations. In the first phase of the project, which ended in July 2014, our main efforts were towards creating new materials (solid adsorbents and membranes) for carbon dioxide capture from flue gases. In many cases, we found that the methodology we had developed in the context of $CO_2$ separations could be applied to other separations. Examples of such spin-offs include separation of $CO_2$ from $H_2$, $CO_2$ from air, $O_2$ from $N_2$, and several separations involving natural gas and mixtures of hydrocarbons.

Below we give a brief summary of some of the main results for each research theme (for a more complete list of highlights, see the CGS website[1]). The numbers in brackets refer to the Center's publications list.

- *Synthesis of nanoporous adsorbents*: The focus of the synthesis group was to develop synthetic strategies for creating new classes of MOFs that enable new mechanisms for gas separations.
    - Synthesis of MOFs with surfaces lined with chelating groups, enabling metal salt insertion [1,2]
    - Bridging ligand substitution for the synthesis of porous molecular cages [1,2]

  - Development of light-responsive MOFs [17]
  - Synthesis of MOFs with large, tunable pore dimensions without interpenetration [11]
  - Methods for functionalizing MOFs with strongly basic amine groups, enabling selective $CO_2$ capture in the presence of water [6,16]
  - Synthesis of MOFs with exposed redox-active metal sites for separating $O_2$ from $N_2$ [3]
  - Utilization of open metal sites in MOFs for the separation of olefins from parrafins [10,20]
  - Synthesis of MOFs with sharply-angled pores for the shape-selective separation of hexane isomers [4]
- *Synthesis of membranes*: Several new classes of membranes have been discovered, based on cyclic peptides [5,8] and on facilitated transport [9,24].
- *Characterization*: We have developed experimental techniques to obtain information on the structure of the materials and on the behavior of gas molecules adsorbed in these materials, in particular:
  - An NMR method to measure dynamics of $CO_2$ in MOFs [22]
  - An NMR technique to measure linker apportionment in MTV-MOFs [21]
  - Novel x-ray techniques to measure molecular orientations in polymer films [7]
  - Novel x-ray absorption spectroscopy techniques to measure directly the effect of adsorbed $CO_2$ on the electronic structure of a porous materials [19]
- *Computational*: We have developed computational methods to obtain a molecular understanding of the properties and performance of the above materials and to make predictions of possible structures that have an optimal performance. The techniques developed include:
  - Computational techniques for screening large databases for potential new capture materials [15] (figure)
  - Very efficient GPU-based molecular simulation software [13,14]
  - Models to understand the $CO_2$ adsorption in amine-functionalized MOFs [23]
  - Combined electronic structure and quantum chemical methods to predict the binding energies of different gases and derive force fields [12,18]

## Future Plans

In the coming four years, the Center will continue developing the most successful aspects of this program, while also extending the approach in certain key directions. In particular, we will pursue several lead discoveries that could potentially result in materials impacting a wide variety of energy-intensive gas separations, including: (i) phase-change adsorbents for low-energy removal of carbon dioxide from flue gas, (ii) redox-active adsorbents for the separation of oxygen from air, (iii) structures with open metal sites for natural gas purification, and (iv) lock-and-key adsorbents for shape-selective hydrocarbon separations. New materials of this type will additionally be integrated Importantly, these new materials will be characterized at the molecular level via in situ gas-dosing spectroscopy and diffraction experiments, combined with computational analysis, and will further be implemented within various new membrane constructs. In addition, we have identified certain gaps in our understanding of the fundamental properties of the new materials under development, namely in controlling crystal size and morphology and in determining the factors governing their mechanical stability. Efforts aimed at gaining a detailed understanding of the atomic-level factors that influence the morphology and mechanical stability of our materials will therefore be introduced.

## Data Management and Open Access

The CGS EFRC is collaborating with LBNL's Materials Genome project to ensure open access to all the structures that are studied in the CGS.

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# Electron-Ion Dynamics with Time-Dependent Density Functional Theory: Towards Predictive Solar Cell Modeling

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**Keywords:** time-dependent density functional theory, coupled electron-ion dynamics, charge-transfer, non-equilibrium, non-adiabatic

**Project Scope:** The goal is to develop a method for electron-ion dynamics in solar cells, using time-dependent density functional theory (TDDFT) for electrons and semiclassics for nuclei, capturing trajectory branching and relaxation in a more theoretically sound way than current methods. Although charge-transfer excitations within TDDFT have been studied somewhat, properties of functionals required for *full* transfer of charge will now be identified and implemented into new approximations, especially for simulations beginning after initial photo-excitation. Semiclassical nuclear dynamics based on the exact factorization of the molecular wavefunction will be developed: the time-dependent potential energy surface (TDPES) incorporates all non-adiabatic electron-nuclear correlation effects.

## Relevance to MGI

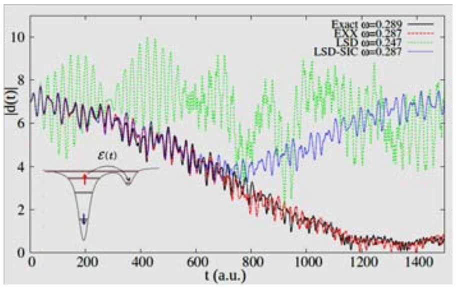
The computational studies that complement the experiments and syntheses of solar cell candidates routinely use TDDFT with Ehrenfest or surface-hopping to model the effect of coupling to nuclei. It is unclear that the exchange-correlation functionals currently used are reliable and accurate enough for charge-transfer processes, and further unclear that the non-adiabatic effects provided by Ehrenfest/surface-hopping are realistic. We are investigating simple models of charge-transfer dynamics for which exact solutions are available, testing functionals and finding essential aspects needed, and finding features of the TDPES that correctly approximate non-adiabatic effects. These models are being used to validate our new method.

## Technical Progress

On the electronic side, we found new step features in the exact correlation potential that do not appear in calculations of spectra, but appear in simulating non-perturbative dynamics, as in solar cells. A step structure associated with the transfer of charge develops, as well as an oscillatory step with a faster time-scale, both of which require non-adiabatic and spatially non-local density-dependence. Lack of these structures in approximations resulted in their failure to transfer charge in a model system, and likely leads to incomplete transfer in realistic systems, explaining results of Nest et al. on small molecules. We derived a decomposition of the potential into a component that depends on the interaction via the exchange-correlation hole, and a component that is kinetic in origin. Although both contribute to the non-adiabatic step, the contribution is often larger in the kinetic term.

We asked whether propagating with the best possible adiabatic approximation, i.e. the exact ground-state functional (“adiabatically-exact”) is good enough to model charge transfer. We found that, despite capturing charge-transfer excitations and ground-state step features in dissociation accurately, adiabatically-exact propagation fails to transfer charge across a model long-range molecule. Charge-transfer *dynamics* is harder for functionals than calculating charge-transfer energies.

Still, ALDA was shown to predict charge-transfer reasonably well (although not fully) in the light-harvesting carotenoid-porphyrin-C60 triad of Rozzi and co-workers, leading us to investigate when the calculation *begins in a photo-excited state*. If the initial Kohn-Sham state is also chosen excited, no charge-transfer step should appear (although an oscillatory step probably remains), so approximations might perform better. Indeed we found that the simple EXX achieved resonant full transfer on a two-electron model. Other functionals however failed, and understanding this led us to uncover a new exact condition on the functional with general implications for time-resolved spectroscopy. A fundamental property is that when a field driving the system is turned off, the system response frequencies are independent of the time at which the field is turned off. The Kohn-Sham potential typically continues evolving, yielding time-dependent Kohn-Sham frequencies. The exchange-correlation kernel must cancel this time-dependence, yielding an exact condition. The condition is typically violated, but we showed that the success of the EXX mentioned earlier is due to its satisfaction.



Dipole moments under weak resonant driving under the respective resonant frequencies, where the amount of transferred charge is inversely related to the degree of violation of our new exact condition.

Regarding coupled electron-ion dynamics, with collaborators from MPI-Halle, we found that quasiclassical propagation of an ensemble of nuclear trajectories on the exact TDPES is accurate in describing branching of a nuclear wavepacket in a model non-adiabatic charge-transfer event in the Shin-Metiu model. Further, we related features of the exact surface to aspects of surface-hopping, like velocity renormalization. We see hints of a force-induced decoherence, but more care is needed to fully analyze this aspect. We then used the exact factorization to define the exact potential acting instead on the electronic system, and compared this to traditional potentials used to study laser-induced electron localization, a technique developed for attosecond control of electrons. Errors in the localization asymmetries predicted by the traditional potential can be explained by features in our exact potential missing in the former.

## Future Plans

We believe that the oscillatory part of the dynamical step structure could be intimately related to the dynamical cancelling of the time-dependence in the Kohn-Sham resonances, as required by the new exact condition. We therefore are urged to model this structure, and the observation above that the kinetic component is often largely responsible for it, suggests we try to utilize an adiabatic approximation for the hole contribution, leaving the more difficult non-adiabatic non-local modeling just for the kinetic contribution, likely within an orbital functional description. We have some preliminary ideas about how to model this, e.g. inputting an expected form of the time-dependent natural orbital occupation numbers, but we have yet to see if it works.

The non-adiabatic step features we studied so far have been in two-electron systems, since we needed to be able to find the exact exchange-correlation potential. It is important to determine the size of these features, and also, the degree of violation of the exact condition by usual approximations, in more realistic systems. As part of this, we have begun a collaboration with Michael Ruggenthaler, Robert van Leeuwen, and their groups. They have developed a code that can find the exact time-dependent Kohn-Sham potential for a given density evolution and initial state for any number of electrons.

The major push regarding the coupling to the nuclei is to develop the semiclassical scheme coupled to TDDFT treatment of electrons, beginning from the exact factorization. Our work so far has been very exploratory since the concepts of the exact potentials and exact geometric phases are quite new, and it has proven useful to study model systems where we can find these exactly to see what the structures that embody exact electron-nuclear correlation look like. Now we are beginning to get a sense of which terms in the equations do what, which terms can be disregarded and which cannot, and are ready to begin developing the practical scheme mentioned in the Scope. We will self-consistently propagate the electronic equation treating the electrons via TDDFT, discarding only those coupling terms we have found are less important, alongside a semiclassical frozen Gaussian type of treatment of the nuclear equation. We will begin with considering just one electron coupled to one nuclear degree of freedom, to make sure that our self-consistent semiclassical scheme still retains branching and decoherence, before moving to more degrees of freedom and more realistic systems.

## Broader impact (Optional for DOE grants/FWPs)

Several postdocs are being trained under this project, developing programming and analytical thinking skills, and awareness of the current challenges in computational materials research. They attend several conferences a year where they are exposed to more applied research groups in computation and experiment, and discuss with others there the challenges and what is needed from the more theoretical side.

## Data Management and Open Access

On our group website, a list of in-home codes are given with a brief description, including which publications of ours use which codes. Viewers are asked to email me to request the code and explain for what purpose. The code will be shared if in a sufficiently stable state.

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# Laminated Elastomeric Composites with Anisotropic Shape Memory

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**Keywords:** Shape memory polymer, elastomer, composite, electrospinning, origami

## Project Scope

Shape memory elastomeric composites (SMECs) are unique in that they are rubbery and soft, yet they have the ability to fix a temporary shape. SMECs previously developed by the PI's (Mather's) group were prepared by embedding a polymer fiber network in an elastomeric matrix, allowing exploitation of the shape memory effect in a low modulus material [1]. The goal of this project is to develop and investigate the thermomechanical properties of an anisotropic SMEC (ASMEC) and its laminates. To allow for scalable manufacturing of SMECs, a thermoplastic polymer system was developed and the fabrication process was modified to comprise of standardized processing techniques. Further, investigations of the ASMECs led to an unexpected finding on the behavior of poly(vinyl acetate) in water, which has led to the study of a water-triggered origami system.

## Relevance to MGI

The development of anisotropic and isotropic SMECs is a highly integrated project involving experimental, theoretical, and computational work. Collaboration between the PIs allows for an in-depth investigation of the structure-function relationship of the materials and for a fundamental understanding of the physics and mechanics that influence observed behaviors. Further, a robust manufacturing process is being developed that utilizes commercially available polymers and industrial processing techniques, enabling rapid market deployment.

## Technical Progress

### *(i) Mechanically Activated Anisotropic Shape Memory Elastomeric Composites (ASMECs)*

ASMECs were fabricated by embedding aligned poly(vinyl acetate) (PVAc) fibers in a crosslinkable elastomer. The aligned fibers were electrospun using a modified setup that included a charged copper plate, which promoted a more uniform electric field, and a rapidly rotating mandrel. Anisotropy was observed in the Young's modulus and reversibly plasticity shape memory (RPSM) properties. In the RPSM cycle, the ASMEC was stretched at room temperature, plastically deforming the PVAc. Upon heating, as the PVAc transitioned from the glassy to rubbery state, contraction of the elastomeric matrix promoted full recovery of the deformation. The shape fixing showed a strong dependence on fiber direction, with decreasing fixing as fiber angle increased from 0° to 90° (0° represents fibers oriented parallel to the stretching direction).

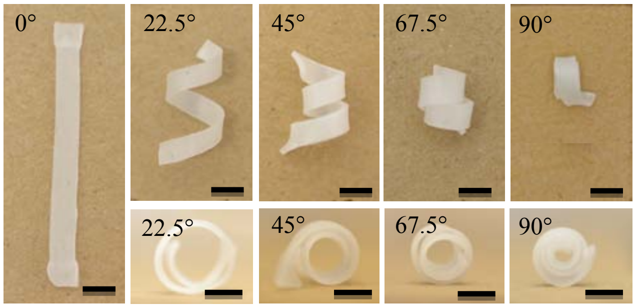

**Figure 1.** Representative images of curled bilayer ASMECs, indicating the pitch in the top row and the radius of curvature in the bottom row. Scale bars represent 4 mm.

Due to the dependence of shape fixing on fiber orientation, we expected that laminated ASMECs with varying fiber orientations would curl after stretching at room temperature. Bilayers were prepared with fibers in one layer oriented at 0° and fibers in the second layer at an angle between 0° and 90°. Curling was observed after stretching, and the pitch and curvature showed a dependence on fiber orientation (Figure 1).

### (ii) *Dual-Spun Thermoplastic Shape Memory Elastomeric Composites (SMECs)*

This research focuses on a new SMEC fabrication method using strictly thermoplastic polymeric components. A thermoplastic elastomer and a semicrystalline polymer (capable of fixing a temporary shape) are simultaneously electrospun, following which the mat is compression molded into a film. This approach has the advantage of control over the relative weight fractions of the two components. By adjusting the flow rates of each polymer solution, the properties of the SMEC can be tuned to meet material requirements. It has been shown that the thermomechanical and shape memory properties systematically vary with composition. In the case of the poly(ε-caprolactone)

(PCL)/Pellethane® 5863-80A system currently studied, the modulus and ability to fix a temporary shape increase with increasing PCL content. It is thought that this fabrication method can be easily scaled for industrial processes.

(iii) *Water-Triggered Origami with a Polymeric Web*

In our ASMEC work, we observed that PVAc fiber mats shrink to less than half of their original size upon hydration. Forces exerted on the polymer fibers during electrospinning, induce molecular alignment along the length of the fibers and leave residual stresses in the vitrified polymer. Thus, when heated above its transition temperature, electrospun PVAc shrinks. Due to the plasticization effect of water in PVAc, the transition temperature of hydrated PVAc fiber mats is lowered below room temperature, allowing molecular reconfiguration to occur after hydration.

Due to the hydrophobic nature of PVAc, water does not readily spread along the surface of PVAc fibers. Therefore, drawn lines of water on one side of a fiber mat localize the shrinkage and lead to folding. Through strategic placement of the water lines, 3D geometries that more closely mimic traditional, paper-based origami can be constructed.

## Future Plans

(i) *Mechanically Activated Anisotropic Shape Memory Elastomeric Composites (ASMECs)*

Bilayer laminated ASMECs with different fiber orientations have been investigated and characterized based on their curling behavior. Multilayer (>2) laminated ASMECs will be studied next, and we expect that the multilayer laminate will exhibit chirality, with both twisting and curling behaviors. Additionally, work will be done to develop an electrospinning setup that can align fibers in multiple directions. This setup can be used to electrospin fiber mats with aligned fibers that gradually change orientation from the 0° to 90° (or further) through the thickness of the mat.

(ii) *Dual-Spun Thermoplastic Shape Memory Elastomeric Composites (SMECs)*

The dual-electrospinning process is generic in that it can be used with any electrospinnable polymer. Therefore, the polymer system can be tailored to meet requirements for specific applications. Additional polymer systems will be studied to explore the range of attainable properties. Further, an electrospinning jet containing a third polymer could be added to the electrospinning setup to obtain a triple SMEC. If the two shape fixing polymers have distinct transitions, triple shape memory properties should be exhibited. Finally, we expect that ASMECs can be dual-spun by modifying the electrospinning setup as described previously.

(iii) *Water-Triggered Origami with a Polymeric Web*

We have showed that PVAc fiber mats fold when lines of water are drawn on the surface of the mat. Further, we observed an increased folding rate for thin fiber mats. Next, we want to study how the thickness of the drawn line affects the folding. We expect to observe not only slower folding, but also a decrease in the ultimate fold angle with thinner lines.

## Broader impact (Optional for DOE grants/FWPs)

Several graduate and undergraduate students have contributed to the work described, and as a collaborative and highly integrated project, the students are exposed to and trained in a multitude of materials research areas. As the research is being conducted in an academic setting, the student researchers' group members also benefit from discussion of the projects. Further, the PI (Mather) works closely with local high schools to get high school students involved and trained in materials research, and an outreach program established by members of Mather's group focuses on educating middle to high school aged students on materials research and engineering.

## Data Management and Open Access

Several manuscripts based on the work described are in preparation, and we plan to continue publishing so that the gathered data and knowledge is accessible to the science community.

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## Publications

Several manuscripts are in preparation.

# Graphene based Origami and Kirigami Metamaterials

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**Keywords:** Graphene, Origami, Kirigami, Electronic membranes, Mechanical Metamaterials

## Project Scope

Origami and kirigami, the arts of folding and cutting paper, offer a powerful new pathway to nanoscale materials design. Drawing inspiration from optical and acoustic metamaterials, it is proposed to develop a framework for designing and fabricating atomic membrane origami and kirigami mechanical metamaterials. Using lithographic techniques, graphene sheets will be perforated and cut to create modules with prescribed mechanical properties. These modules will be assembled to create mechanical meta-materials whose response to applied stresses, temperature, and other environmental signals can be tailored.

## Relevance to MGI

Adopting a single platform, graphene, along with cuts following kirigami and origami principles, we can tailor emergent mechanical behaviors so that material properties can be designed. This addresses a major need for materials with tunable mechanical properties for construction of micro- and nano-scale machines. Developing such materials will have fundamental impacts on micro-engineering, enabling the manufacture of a range of components from micron-scale actuators for soft robotics to active biomimetic materials for artificial tissues.

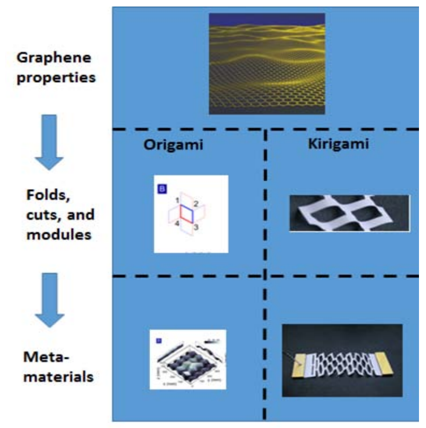

**Figure.** The project is divided into three parts: properties of graphene, basic modules, and metamaterials.

## Technical Progress

Graphene provides an ideal system to test the statistical mechanics of statically rippled and thermally fluctuating elastic membranes. The high Young's modulus of graphene means that thermal fluctuations over even small length scales significantly stiffen the renormalized bending rigidity. We have measured the effect of thermal fluctuations on graphene ribbons of width $W$ and length $L$, pinned at one end, in both experiments and in coarse-grained Molecular Dynamics simulations and compared the results with analytic predictions of the scaling of width-averaged root-mean-squared height fluctuations as a function of distance along the ribbon. A scaling collapse as a function of $W$ and $L$ also allows us to extract the scaling exponent governing the long-wavelength stiffening of the bending rigidity. Various transfer techniques for graphene have been explored so that it can be loaded onto the surface of a Langmuir-Blodgett trough. A custom built trough and Brewster Angle Microscope are under construction that will enable high speed imaging of nanoscale fluctuations in the graphene surface height. An optical interferometric technique for directly imaging height variations in a suspended graphene membrane has been developed. This technique yields nanometer-resolution information about the height of ripples and fluctuation of the membrane as a function of position.

## Future Plans

A full understanding of the geometry-dependent mechanical properties of graphene, including arrays of cuts, is being developed so that we can design a variety of modular elements with desired mechanical properties starting from pure graphene alone. We also plan to measure the Poisson ratio of graphene, predicted to be negative. This would be the first known example of an entropically-driven auxetic material following the membrane paradigm. Work is also underway to create single-crystal graphene membrane structures instead of the polycrystalline ones that have been studied to date. In addition, experiments are planned to probe the stability and fluctuations between different metastable states of the kirigami structures.

**Broader impact (Optional for DOE grants/FWPs)**

On Dec. 6, 2014 a one day New York Complex Matter Workshop was held at Cornell on the theme of constraints, graphene and kirigami with a set of speakers very relevant to the project. There were over 100 participants from 5 different universities, including Syracuse, Cornell, New York State University at Binghamton, The University of Rochester and Rochester institute of Technology. We have also started with the preparation of our proposed scientific voice workshops. A demo of the workshop that can be found at: http://cohengroup.lassp.cornell.edu/media.php?show=34

**Data Management and Open Access**

This collaborative project (CSH: Cornell-Syracuse-Harvard) will generate a diverse set of theoretical, computational and experimental data that will be of interest to communities in materials science, physics, engineering and chemistry. To unite the diversity in data type and geographical spread of the CSH team, a centralized computer facility for data storage and access will be created. The computer cluster will be housed in the Green Data Center at Syracuse University, and managed by the Syracuse University Information Technology and Services group. This server will be backed up daily on offsite servers at partnering institutions. Individual research groups will be provided password-protected access to the cluster to store and save their data. The team will follow strictly the NSF guidelines related to the data management procedures. No personal protected information of any type will be used and all results of the proposed fundamental research are intended for broad dissemination through publications and presentations.

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# Multiscale Design of Hard and High Temperature Resistant Coatings by Computation and Experiment.

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**Keywords:** High temperature coatings, hard coatings, thermal barriers, ab-initio molecular dynamics, distinct element method simulations.

## Project Scope

The goal of this collaborative research is to design and develop a new class of protective (Zr,Si)B-C-N coatings, coalescing computational investigation and experimental realization and characterization. Applying a hard coating, which bonds strongly to the surface of the material, prevents excessive abrasion and provides the needed shield towards mechanical impacts. At high temperatures and in an oxidative environment, however, many hard coatings quickly deteriorate due to thermal instability and chemical degradation. Thus, there is a need to develop hard, thermally stable and oxidation resistant coatings for high temperature (>1500$^{o}$ C) applications.

## Relevance to MGI

The project couples multiscale computations and experiment to merge the high-temperature oxidation resistant properties of Si-B-C-N and high hardness properties of Zr-B-C-N systems. The predictive effort spans from atomistic to multiscale distinct element method simulations to formulate solid predictions of the optimized compositions. These predictions provide critical guidance for synthesizing coatings with targeted properties (hardness and high temperature oxidation resistance). We expect that in these new coatings, the desirable properties will coexist, resulting in a new generation of protective layers.

## Technical Progress

Our HRTEM characterization studies of amorphous Si-B-C-N coatings showed that these coatings remain amorphous when annealed to 1700$^{o}$ C in air and exhibit an extraordinary oxidation resistance.[1] The high temperature oxidation resistance is attributed to formation of an outer amorphous $SiO_2$ layer and an inner nano composite layer of finely distributed h-BN nano crystals embedded in an amorphous $SiO_2$ matrix. Molecular dynamics simulation studies confirmed this hypothesis, Fig. 1, and now it is looking at possible ways to further maximize these properties.

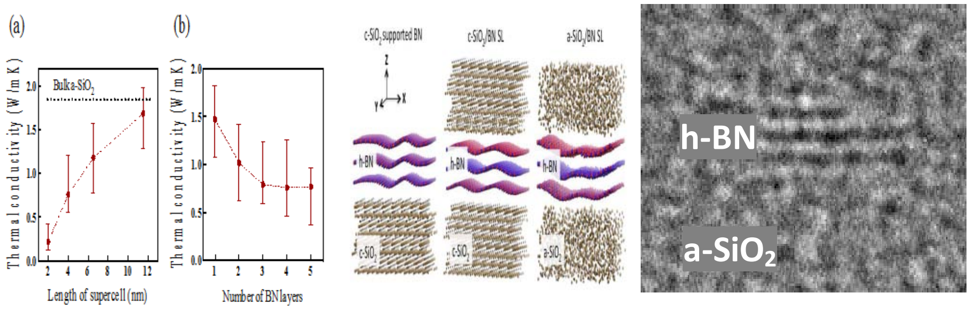

**Figure 1.** Molecular dynamics predictions of the cross-plane thermal conductivity as a function of the number of BN layers, which are embedded in an amorphous-$SiO_2$ (left) indicate flattening above 3-layers (middle). HRTEM image (right) of the corresponding synthesized h-BN $SiO_2$ structure.

Molecular dynamics investigations are addressing the fundamental issue of combining desirable properties by varying chemical composition and structure. We have focused onto the impact of structure onto the thermal properties. We have computed the thermal conductivity and thermal contact resistance between h-BN and $SiO_2$. Remarkably, we found that a single BN layer (~1 nm) provides the same thermal resistance as a 60 nm thick a-$SiO_2$. Thus, BN interfaces can be used as efficient thermal insulators. We also found ultra-low thermal conductivities of BN/a-$SiO_2$ in the 0.22 to 1.68 W/mK range which could be tuned by the number of BN layers, Fig. 1. Additionally, the calculated low-thermal conductivities are not dependent on temperature, and are robust up to 2000 K. These important results provide key information for the nanoscale structure of high temperature thermal barrier coatings, Fig. 1.

A series of Zr-B-C-N coatings were synthesized experimentally. Surprisingly, a slight change in the $N_2$ content in the plasma was found to result in tremendous differences in the oxidation resistance, hardness and electrical resistivity. The structure of the coatings also varied from nanocolumnar ($Zr_{61}B_{27}C_6N_3$) to an entirely amorphous-like structure ($Zr_{24}B_{19}C_6N_{49}$). The $Zr_{41}B_{30}C_8N_{20}$ coating was found to possess the highest hardness (37 GPa), modulus (317 GPa) and electrical conductivity (electrical resistivity of $1.7 \times 10^{-6}$ Ωm). The coating consists of nano-needle structures which have a length of about 40 nm and a width of ~10 nm. The nano-needles have a fcc structure and are composed of ZrN and/or Zr(B,N) nano-domain structures (~2 nm) that are semi-coherently joined via Zr-N monolayer interfaces, Fig. 2. The formation of ZrN and/or Zr(B,C,N) nano-domain structures, semi-coherently joined via Zr-N monolayer interfaces within the nano-needle structures, play a critical role in achieving the high hardness and modulus. We used ab-initio molecular dynamics simulations to obtain a first insight into the structures of Zr-B-C-N coatings with compositions similar to those that were synthesized experimentally. We used a melt-quench approach to generate at least six configurations for each composition each with 100 atoms in the simulation box. Interestingly, we detect rapid formation of small nuclei which are characteristic of a nanocrystalline structure rather than amorphous. The pattern formation and ordering were found to resemble those observed experimentally, Fig. 2. More importantly, we computed elastic constants for a variety of models and the results showed, very clearly, that the $Zr_{42}B_{30}C_8N_{20}$ composition has the highest hardness (8 GPa) among all the rest compositions. The trend corresponds nicely to experimental data, which also identifies a similar composition as the one with the highest hardness.

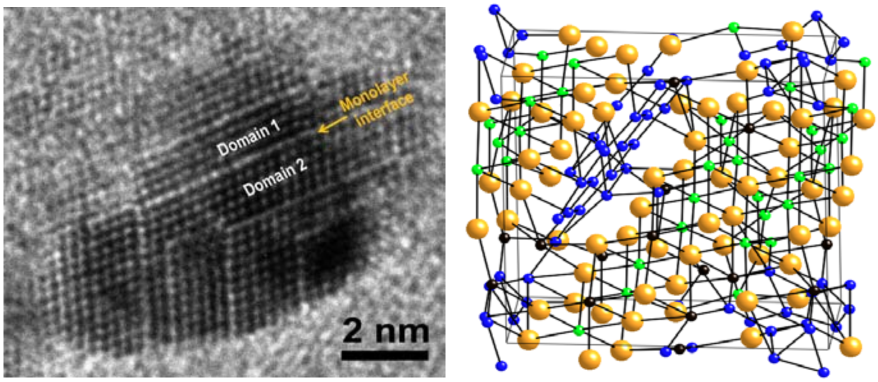

**Figure 2.** HRTEM image of a nano needle in the $Zr_{41}B_{30}C_8N_{20}$ film showing nano domains separated by monolayer interfaces and the simulated structure for $Zr_{42}B_{32}C_8N_{18}$ resembling the experimental structure.

## Future Plans

Having understood the effect of nano-structure on the thermal properties, a part of the future simulation work will address the effect of the chemical composition. The next focus will be on enhancing mechanical properties since the goal is to develop new coatings in which the desirable properties coexist in both thermal and mechanical domains. Our preliminary molecular dynamics studies showed that adding $Si_3N_4$ ti ZrBCN reduces the elastic properties and decreases the hardness of the structures. However, addition of $Si_3N_4$ to ZrBCN has been proposed to increase high temperature oxidation resistance. It is anticipated that this will come to an expense of a reduced hardness of the coating but determining an optimum compromise between hardness and oxidation resistance is worth exploring. In recent studies, we found that replacement of Zr by Hf presents a high potential alternative for these coatings and thus, we included Hf-Si-B-N coatings in our portfolio. More specifically, multiscale simulation and mechanical behavior will determine: (1) Thermal properties and Hardness of $Zr_{50}B_{50-x}N_x$ (explore compositions x= 20, 25, 30); (2) Thermal and mechanical properties of $(Zr_{1-x}Si_x)B_{1-y}N_y$; (3) Thermal and mechanical properties of $(Hf_{1-x}Si_x)B_{1-y}N_y$.

Following the theoretical predictions, compositions of (Zr,Si)BN and (Hf,Si)BN coatings presenting attractive combination of properties will be synthesized and their structures and properties characterized experimentally in order to accelerate coating development.

### Broader impact

The focus of this research - the discovery of new coatings working under extreme conditions - can find application in multitude of critical components such as turbine blades, reusable launch vehicles, hypersonic vehicles, and thermal barrier applications. The research program is integrated with a multi-layered education and outreach program involving curricula development, exposing students to a novel interdisciplinary field, and summer camps. At UTA, two female Ph.D. students (one in materials science and one in chemistry) have taken their dissertation research on the project. A Postdoc was also involved under the supervision of co-PI Kroll in Chemistry department. PI (Meletis) and Co-PI (Jiang) have been involved in the UTA College of Engineering ***2014 Entry to Engineering Camp*** (July 15, 2014, with 50 coed 6th - 8th grade students), ***College of Engineering 2014 summer camp for Girlgeneering*** (July 29, 2014, with 50 5th-9th grade girls) and ***2014 American Society of Materials Summer Camp*** (July 19, 2014, 33 students from 11 to 17 years old). At UMN, one graduate student, one undergraduate (Hispanic), and one post-doc are directly involved in this work. The results obtained in this researched enriched the well-attended Computational Nanomechanics course developed by Dumitrica. Also, at UMN undergraduates from Pi Tau Sigma Honors Society are engaged in activities of the American Ceramic Society, including the UMN version of the Ceramic Mug Drop Contest.

### Data Management and Open Access

Ab-initio molecular dynamics simulations are using the Vienna Ab Initio Simulation Package that is a commercially available program. VASP produces a single formatted ASCII output file containing the metadata of initial structure, program parameters, and results relevant for further analysis. For modeling of amorphous structures an in-house code (Continuum Random Network Generator, CORANGE) is used. CORANGE produces ASCII data that can be easily stored. Both of the above data are stored in the project data and are publically available. The force-field development is using the Tersoff-potential as well as the REAX-ForceField approach. Both potentials are implemented in the LAMMPS package available from Sandia National Laboratory. Mesoscopic mechanical simulations are performed with the code PFC3D provided by Itasca Inc. All the developed parameters for the atomistic potentials, such as the Lennard-Jones parameters needed to describe the complex interactions between boron nitride and silica, as well as the parameterization of the contact models for the PFC3D, are reported in our publications. The mesoscopic part of the distinct element method working with PFC3D is freely available via the Office for Technology Commercialization, University of Minnesota. All experimental synthesis and characterization data are stored in the project data and are also available for access.

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# Next-generation Nanostructured Polymer Electrolytes by Molecular Design

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**Keywords:** batteries, lithium, polymer electrolytes, synthesis, screening, computation, modeling.

## Project Scope

The objective of our project is to develop safe, robust, and efficient nanostructured polymer electrolytes for large-scale lithium batteries used in electric vehicles and grid applications. Our approach is based on the MGI approach wherein we combine expertise in theory and simulation, polymer synthesis, and polymer electrolyte characterization, to facilitate accelerated discovery of new polymer electrolytes. State-of-the-art theoretical and coarse-graining methods drive the screening and design of new polymer electrolytes, as well as provide the detailed understanding of ion diffusion mechanisms. Figure 1 shows strong correlation between modeling and experimental results for the lithium conductivity in a series of carbonyl- and either-containing polymers. Our tangible goal is to develop a polymer electrolyte with conductivity larger than that of the current state-of-the-art polymer electrolyte (PEO).

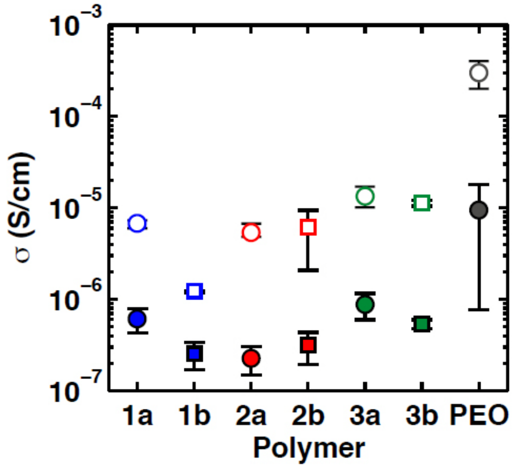

**Figure 1.** Comparison of experimental measurements of lithium salt conductivity (cation+anion; open symbols) and simulated results of lithium ion conductivity (filled symbols) of a series of carbonyl- and ether-containing polymer electrolytes at 90 °C. Anion conductivity has not yet been modeled.

## Relevance to MGI

Our approach fully embodies the MGI approach and consists of a cyclic, iterative process wherein a series of carbonyl- and ether-containing polymer electrolytes are synthesized by the Coates group, characterized by the Balsara group, and modeled by the Miller and Wang groups. Our modeling approach has recently been validated by experimental measurements, as shown in the Figure. We have now begun to predict ion transport in materials that have not yet been synthesized. Promising polymer electrolyte candidates identified by theory will then be synthesized in the laboratory, and their ion transport characteristics will be measured. We are thus about to embark on the second and more exciting MGI iteration.

## Technical Progress

A series of polymers with carbonyl and ether oxygens shown in the Figure 2 with similar molecular weights were synthesized by the alternating copolymerization of cyclic anhydrides and epoxides. The robustness and functional group tolerance of the Co (III) catalysts allowed us to systematically vary the polymer backbone and side chains. This allowed us to investigate the effect of different functional groups and architectures on ionic conductivity and other polymer properties. We chose these groups because liquid electrolytes in current lithim batteries contain carbonyl groups while the current polymer electrolyte contains ether groups. These initial targets were based on intuition but without the benefit of the MGI approach. The samples were shipped to Berkeley. Electrolytes were prepared by homogeneous mixing of the polymers and lithium bis(trifluoromethanesulfone)imide (LiTFSI) salt. Films of the electrolyte were made by solvent casting in an argon-filled glove box and cells for conductivity measurements were prepared using stainless steel plates as electrodes. The assembly was sealed in a pouch cell in the glove box, and ionic conductivity was measured using a potentiostat. The measured conductivites at 90 oC are shown in Figure 1.

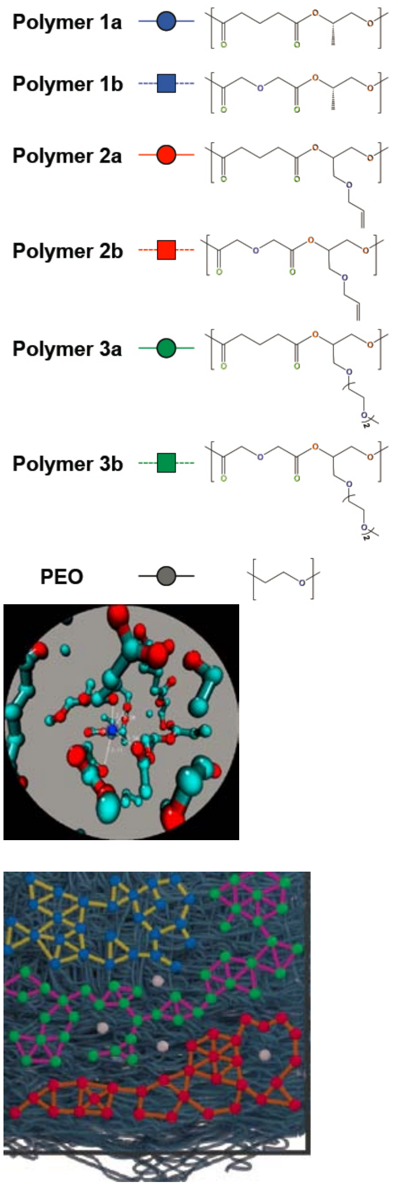

**Figure 2.** Top: Polymers used to begin the MGI iteration. Middle: Typical simulated solvation shell of lithium ions. Bottom: Connectivity osolvation shells

The data shown in Figure 1, while providing validation of the theoretical model, also shows the futility of targets based entirely on intuition: the conductivity of the new polymers were about an order of magnitude lower than that of poly(ethylene oxide) (PEO), the best available electrolyte to date. Our modeling effort enables mechanistic insight into the reason for the low conductivity of these newly developed electrolytes. The simulations were used to determine motiffs that solvate the lithium ions. An example of a solvation shell is shown in Figure 2. The diffusion of lithium ions is affected not only by the probability of the spontaneous formation of solvation but connectvity across solvation shells. A key distingushing feature of PEO from the six polymers that we synthesized is the connectivity of solvation shells.

The insight developed from the comparative studies and mechanistic analysis of the polyesters as well as PEO has been used to develop a coarse grained model that will be used to effectively screen a large number of candidate polymers. In particular, we have found that ion transport in polymers can be modeled as hopping on a dynamical network of sites. The distribution of sites and associated transition rates are characteristic properties of the polymer, which can be assessed with short molecular dynamics simulations. This model also highlights our design strategy that molecular design of monomer structure can be used to create favorable site distributions that facilitate more efficient ion transport.

## Future Plans

Our modeling effort so far has pointed to striking differences in the solvation shell structure between PEO and other carbonyl- and ether-containing polymers. In particular, both the MD and coarse-grained simulations suggest that intra-chain rather than inter-chain binding of the Li+ by the oxygen groups allows more facile Li+ motion. This insight will be exploited to suggest new carbonyl- and ether-containing polymers whose solvation structure is more akin to PEO. A series of candidate polymers will be first screened by our modeling effort. The candidates with the most promising ion conductivities will then be synthesized and characterized.

### Broader impact (Optional for DOE grants/FWPs)

Our project provides an ideal platform for training and educating students and postdoctoral researchers in the area of materials research and education. Being a fully integrated theory-synthesis-characterization project, the students and postdoctoral scholars are exposed to and involved in all three aspects of the research. A web-based discussion group has been set up where these junior researchers are regularly (on a weekly basis) discussing research progress, exchanging ideas, analyzing results and planning the next stage. In addition, all-hands web-based meetings are held once a month where students or postdocs from each of the groups give a presentation of the newest results. These experiences help prepare the students and postdocs involved to acquire the interdiscipline, teamwork, leadership and communication skills as the next generation of material researchers.

### Data Management and Open Access

A primary goal of this DMREF project is to broadly disseminate our findings to interested parties. A primary mode for achieving this aim will be through publication in peer-reviewed journals. However, we will also develop and maintain a web-based Polymer Electrolyte Archive for the duration of the proposed research that will allow outside parties to directly access and download posted experimental and simulation data. Compiled experimental and simulation data will be uploaded by the four collaborating research groups, using password protection. All posted data will be available to the general public for download, without password protection. Data will be released to the website after it is accepted for publication, and the appropriate citations will be indicated on the website. The source code for all programs that are written as part of this DMREF project will also be made available on the Polymer Electrolyte Archive.

# Design of Nanoscale Alloy Catalysts from First Principles

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**Keywords:** Nanoparticle, catalysis, $CO_2$ reduction, hydrogen evolution

### Project Scope

We are developing and validating a way to design nanoparticle alloy catalysts using density functional theory and the cluster expansion approach. The computational approach is iteratively improved by comparing computational predictions with experimental results on the structure and catalytic properties of nanoparticles. To demonstrate and evaluate our approach, we are designing Cu-alloy catalysts for $CO_2$ reduction.

### Relevance to MGI

The predictions generated by our computational models are being compared to experimental data on alloy nanoparticle catalysts. Based on these comparisons, we are iteratively refining both our computational approach and synthesis methods to improve our ability to make reliable predictions that can be used for nanoparticle design. Towards this end, we are developing methods to predict both how synthesis methods affect nanoparticle structure and how nanoparticle structure affects catalytic activity, stability, and selectivity.

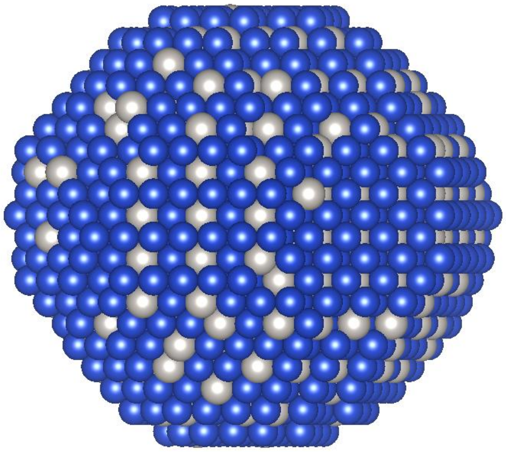

**Figure 1.** A representative structure for a ~4 nm $Cu_{1800}Pt_{600}$ nanoparticle at room temperature as predicted using the cluster expansions generated in this project. Blue spheres represent Cu, and grey represent Pt.

### Technical Progress

We have generated preliminary cluster expansions for Cu-Ni and Cu-Pt nanoparticles. We are currently using these cluster expansions to predict the equilibrium structures of these nanoparticles (Figure 1). In parallel, we have been synthesizing and electrochemically testing Cu-Pt nanoparticles. Our initial focus has been on the hydrogen evolution reaction, as suppressing unwanted hydrogen evolution is one of the primary challenges in developing catalysts for $CO_2$ reduction. Because the mechanisms for the hydrogen evolution reaction are relatively well understood, the study of this reaction also provides a valuable benchmark for evaluating our ability to predict the catalytic activity of alloy nanoparticles. We have begun a series of calculations to evaluate how local atomic order on the Cu-Pt surface affects catalytic activity for hydrogen evolution.

### Future Plans

This project has two primary thrusts. In the first, a predictive model that relates synthesis conditions to nanoparticle structure is being developed and validated. We have constructed cluster expansions, trained on density functional theory calculations, for Cu-Pt and Cu-Ni nanoparticles. We are currently using these expansions in Monte Carlo simulations to predict the equilibrium particle structures. These predictions will be compared to the experimentally-determined structural characteristics of monodisperse and homogeneous alloy nanoparticles created from organic solution synthesis. The computational and experimental approaches will be iteratively refined to approach consistency. For example, we will explore the extent to which it is necessary to anneal the synthesized particles to bring their structures into agreement with those predicted through simulated annealing.

In the second thrust, a predictive model that relates nanoparticle structure to catalytic properties is being developed and validated. Our initial focus is on the hydrogen evolution reaction, which is known to compete with the $CO_2$ reduction reaction on catalyst surfaces. We are using density functional theory calculations to calculate the binding energies of hydrogen on different sites of alloy nanoparticle surfaces, as it has been demonstrated that hydrogen binding energy is a useful descriptor of catalytic activity for hydrogen evolution on extended surfaces. In parallel, we are generating experimental data on the catalytic properties of nanoparticles of different sizes, compositions and structures for hydrogen evolution. By comparing the calculated hydrogen binding energies with the experimental data, we will develop predictive models for the activity Cu-alloy nanoparticles for hydrogen evolution as a function of particle composition, size, and structure. We will then extend this approach to develop a similar predictive model for $CO_2$ reduction, with the goal of finding nanoparticles that are active for $CO_2$ reduction while suppressing hydrogen evolution.

The combination of the above thrusts will enable the predictions of how synthesis conditions affect alloy nanoparticle structure and how the structure relates to catalytic activity. We will integrate these thrusts to determine the synthesis steps that are most likely to produce nanoparticles with high activity, selectivity, and stability. These predictions will be validated experimentally.

**Broader impact (Optional for DOE grants/FWPs)**

The development of viable catalysts for $CO_2$ reduction could enable the synthesis of hydrocarbon fuels from $CO_2$ powered by off-peak electricity, simultaneously increasing global fuel supply and reducing one of the primary causes of global warming. The PIs meet regularly with the Ph.D. students working on this project to mentor them and discuss research results and strategies. The project team will include a female high school student from a largely minority Baltimore City public school, who will gain valuable research experience by working closely with the graduate students and PIs. To educate students on modern challenges and potential solutions in the field of energy-related technologies, we will develop a course on renewable energy technologies for undergraduate and graduate students at Johns Hopkins University. The goal of this course will be to train the next generation of scientists and engineers in modern computational and experimental approaches to addressing the global challenges in energy and environmental sustainability. To further educate students and other interested parties about renewable energy, a "Renewable Energy Technologies" workshop will be held at Johns Hopkins University, with the content designed to disseminate leading-edge scientific and technological knowledge about energy sustainability.

**Data Management and Open Access**

The computational and experimental data generated during this project will be archived and made available for sharing, as will the computational tools developed for this project. Detailed descriptions of the computational and synthesis methods used will be published in peer-reviewed literature and student theses.

**Publications**

No publications to date.

# Predictive Theory of Transition Metal Oxide Catalysis

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**Keywords:** heterogeneous catalysis, surface chemistry, oxide chemistry, *ab initio* methods, benchmarking

### Project Scope

The scope of this project is to establish a fundamental understanding of oxide surfaces to a level where electronic structure-based simulations can be utilized to quantitatively predict the catalytic properties (activity and selectivity) for key reactions relevant for energy conversion. A key element in the project is to establish the accuracy of theoretical methods.

### Relevance to MGI

We are developing accurate and efficient electronic structure calculations for surface chemistry. Efficiency is an essential parameter since the methods must be able to treat surfaces of complex heterogeneous catalysts and do so fast enough to produce substantial amounts of data than can be made available for catalyst design. Accuracy is equally essential, and due to lack of "exact" computational solutions for complex oxides, we benchmark the electronic structure methods against carefully designed experiments including accurate syntheses of well-defined surface structures of metal oxides, detailed characterization using synchrotron methods and the free electron laser at SLAC, and the most accurate measurements of adsorbate-surface interaction energies available to date.

### Technical Progress

The Random Phase Approximation (RPA), combined with exact change (EXX), is a non-empirical beyond-DFT method that generally improves the exchange-correlation (xc) energy. However, it is extremely computational demanding. We have ported the RPA method on graphic processing units (GPUs) and gained a speed up of 40x.[1] This implementation was applied to benchmark bulk formation enthalpies of group I and II metal oxides,[2] and 3*d* transition metal oxides.[3] The EXX+RPA results were compared to a hierarchy of xc functionals. Our results show that deviations from experiments can be separated into two parts: a systematic and uniform error related to the O reference energy and the errors specific to different oxidation states. We find that EXX+RPA improves both.

As a first step towards a database of adsorption and activation energies for oxide surfaces, we performed a theoretical investigation of surface properties and energetics of molecules and oxygen chemistry on low-Miller index surfaces of alkaline-earth metal oxides (MgO, CaO, SrO, BaO).[8] The accuracy of commonly used xc functionals and RPA was evaluated and compared to experiments. All considered functionals qualitatively predict similar adsorption energy trends and the calculated and experimental adsorption energies lie within the bounds of LDA (too high) and RPBE (too low). The ordering between adsorption energies on different surface facets is attributed to the local geometrical and electronic surface structure of the metal constituent of the oxide.

We used microkinetic modeling together with the recently developed BEEF-vdW xc functional, which utilizes the Bayesian approach to statistics to quantitatively estimate the error on DFT energies using "ensembles" of energies that reproduce known errors in DFT calculations and capture correlations between these errors, to assess the impact of uncertainty in energetics on predicted catalytic rates.[5] We find that the error on rates exhibits a nontrivial dependence on reaction condition and catalytic surface, but despite relatively large errors in DFT energetics(~0.2 eV) the error on predicted turnover frequencies(1-2 orders of magnitude) is smaller than expected.

We have worked to extend the *ab initio* nanoreactor to problems involving heterogeneous catalysis with the first target to explore the Fischer-Tropsch reaction on iron and iron/silica for direct nonoxidative conversion of methane to ethylene, aromatics and hydrogen.[I] The basic idea of the nanoreactor is to use *ab initio* molecular dynamics to sample the space of chemical reactions,[II] which are monitored by pattern recognition algorithms. We added effective core potentials (ECPs) to describe the metal atoms to our GPU-based code, which required development of a GPU-based algorithm for the ECP integrals. We also incorporated fractional occupation in the self-consistent field procedure to be able to sample several spin states, necessary when modeling metal clusters. Finally, we incorporated new boundary conditions for a surface nanoreactor – augmenting the spherical nanoreactor with a disc-shaped region representing the surface not subject to periodic confining potential.

A key element in testing new computational approaches for oxide surface chemistry is to compare their results to accurate experimental adsorption energies for well-defined systems. Currently we are utilizing the capability to directly measure heats of interaction of adsorbed species on single crystal oxide surfaces using single crystal adsorption calorimetry (SCAC) provided by only one group in the US. We have applied it to study energies of several species on well-defined oxide surfaces. Specifically, the adsorption energies of $H_2O$ and $D_2O$ on NiO(111) and $Fe_3O_4$(111) have been measured. Currently we are in the process of analyzing our findings.

**Future Plans**

DFT calculations beyond the standard generalized gradient approximation (GGA) have only been carried out on a limited number of reactions on extended oxide surfaces. Our study of alkali-earth metal oxides[8] serves as a platform for understanding more complex transition metal oxide surfaces. In the next step, the developed infrastructure and gained knowledge will be used to study the surfaces of 3*d* transition metal surfaces in the rock-salt type structure with different levels of DFT and beyond. We will also initiate the benchmarking of more complex oxides, which will include some of the experimentally studied oxides systems within the project. Based on these findings we will continue contributing to the development of a database containing oxide surface energetics that can be used for understanding oxide catalysis and eventually for metal oxide catalyst design.

The newly developed nanoreactor scheme enables us to treat systems with different boundary condition in particular a spherical nanoreactor vessel with a disc-shaped region, which can represent a surface that is not subject to the periodic confining potential. We will perform simulations of both the Fischer-Tropsch reaction (using an iron nanoparticle with $\approx$50 atoms to represent the iron surface) as well as simulations of methane activation by silica with single iron atom substitutional defects.

We will continue our SCAC studies of adsorbed $H_2O$ and $D_2O$ on NiO and $Fe_3O_4$. Previous surface science studies of water interaction with $Fe_3O_4$(111) showed that, while it adsorbs molecularly at 100 K, at higher temperatures it dissociates with high probability to produce adsorbed OH groups. When measuring heat of reaction of $D_2O$ with NiO(111) at temperatures 100-300 K, we found that water adsorbed only molecularly, and did not dissociate to produce OH as expected from previous reports (although some other papers had conflicting results that agree with our results). We will elucidate why the expected chemistry did not occur. We are now pursuing measurements of heats of dissociative adsorption of methanol and formic acid on $Fe_3O_4$(111), to produce surface methoxy and formate species, respectively, along with adsorbed OH.

Using ambient pressure synchrotron X-ray photoemission spectroscopy, we studied the adsorption of polar adsorbates at surfaces of the $LaAlO_3/SrTiO_3$(100) heterostructure, a system with conducting interface between the two band insulators.[IV] Dissociative water adsorption at the surface Al atoms results in significant band. In addition, we have demonstrated that one can tune the interface dipole between the heterostructure layers. These results demonstrate that oxides on the atomic scale can be uniquely employed for tailoring band alignments, which opens possibilities to control band alignments at functional devices for photoelectrochemical applications. While this work was largely supported outside of the MGI program, we note that we have recently established the ability to release millimeter-scale free-standing oxide films which are nanometers in thickness. This should provide the ideal platform for thermodynamic measurements of adsorbates within the MGI collaboration.

## Data Management and Open Access

Our GPU implementation of RPA in the GPAW code is publicly available on the website https://wiki.fysik.dtu.dk/gpaw/devel/projects/gpu.html. This GPU version shows a speedup of 40 (GPU vs. CPU+GPU) making GPUs about a factor of 5 more cost effective for RPA calculations.

All by us published oxide surface chemistry data will be made publicly available through CatApp. CatApp[III] is a web application that provides public access to DFT-calculated reaction and activation energies. It is based on a Javascript API, which is available and downloadable through our web service http://slac.stanford.edu/~strabo/catapp/CatApp.html. In addition, we have made it possible for anyone to contribute by uploading their data at http://slac.stanford.edu/~strabo/catapp/Upload.html.

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# Design of Novel Sodium Superionic Conductors using Integrated High-throughput First Principles Calculations, Data Mining and Experiments

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**Keywords:** sodium superionic conductor; first principles diffusion; pulsed electric current sintering; interface engineering; multivariate time series analysis

### Project Scope

The aim of this project is to design and optimize novel sodium superionic conductors using a data-driven approach that tightly integrates high-throughput first principles modeling, data mining, synthesis and characterization, and interfacial engineering. Our target is to develop materials that have $Na^+$ conductivity in excess of 1 mS $cm^{-1}$ at room temperature, with either intrinsic stability against typical 4.5V cathodes and anodes, or forming a stable ionic conducting solid-electrolyte interphase (SEI).

### Relevance to MGI

This undertaking would require significant advancements on several fronts: (i) the development of robust computational frameworks to manage long-running first principles transport simulations; (ii) the design of an efficient database schema for the storage of truly “big materials data” arising from these simulations; (iii) the innovative application of multivariate time series machine learning techniques to extract scientific insights and trends; (iv) the use of advanced methods to synthesize and characterize candidate sodium superionic conductors; and (v) the model-based engineering of interfaces to mediate interfacial bottlenecks and enhance $Na^+$ conductivity.

### Technical Progress

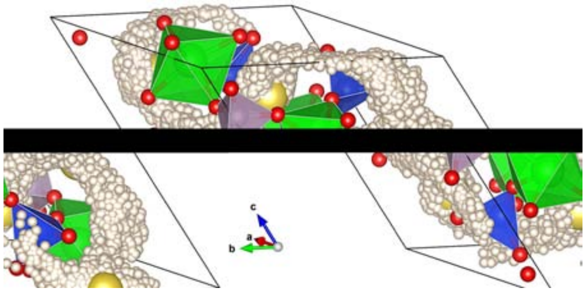

Fig. 1: Diffusion pathway in NASICON ($Na_3Zr_2Si_2PO_{12}$) structure from AIMD simulations.

We have adopted the Natrium Superionic Conductor (NASICON)[1] as an initial prototype structure for the development of the necessary computational and experimental infrastructure for this project. A superionic conductor database and a beta graphical user interface (GUI) have already been developed for the sharing of computed material property information within the team. We have also developed a new computational framework have been developed to support automated ab initio molecular dynamics (AIMD) simulations utilizing idle computing resources at the San Diego Supercomputer Center. This framework has been robustly tested on tens of AIMD simulations in the past few months, and is currently being utilized for detailed investigations of the NASICON family of structures (Figure 1). On the experimental front, preliminary studies show that a special processing route can more than double the $Na^+$ conductivity of the NASICON to achieve a high conductivity of 0.69 mS $cm^{-1}$ at room temperature. Further analysis suggests partial stabilization of the high-temperature and high-symmetry phase, which may explain the enhanced conductivity.

### Future Plans

The overall research plan comprises **four key tasks**. We will conduct a broad-based evaluation of all known alkali-containing oxides, sulfides and oxysulfides for $Na^+$ conductivity, electrochemical stability, phase stability and aqueous stability using high-throughput first principles calculations and topological analysis. Data mining techniques will be applied on the large property database generated to elucidate structural-chemistry-property relationships. Using these insights, we will apply structure prediction algorithms to generate novel materials. In parallel, multi-property screening of the computed materials will be conducted, and the most promising sodium superionic conductors would then be synthesized, characterized and optimized experimentally. In-depth first principles investigations will also be carried out to complement experimental efforts on the most promising materials.

Efforts are underway to understand the sodium diffusion mechanisms in the NASICON structure and develop doping strategies to further enhance $Na^+$ conductivity. Using this preliminary data, we are developing data mining approaches to analyze trajectory information from AIMD simulations, with the hope of extracting insights into correlated diffusion events for subsequent analysis. Based on the initial experimental results, we will investigate the exact mechanisms of enhanced conductivity observed in the NASICON structure both experimentally and using first principles calculations, and further improve this effect. Subsequently, we aim to extend similar (and/or develop new) processing and interfacial engineering strategies to improve the conductivities of other predicted $Na^+$ super ionic conductors.

### Broader impact

The success of the project will lead to safer, higher energy density storage based on all-solid state Na-ion batteries. More broadly, it will also serve as a model framework for similar efforts in other technological areas. As a part of public outreach efforts, co-PI Meng’s group intends to develop hands-on-modules to learn about sodium transport in solid-state devices. Undergraduate students will be included in this project to foster the culture of performing original research work. Also, efforts will be taken to involve underrepresented groups. The PIs will give public lectures at various MGI forums, “Connect San Diego”, “CleanTech San Diego” and the annual weeklong summer institute hosted by the San Diego Supercomputer Center. PI Ong will also develop a new course on “First Principles Materials Design” from which course materials will be made publicly available. The HT computational frameworks and materials analysis in this DMREF will be made open source as add-ons to PI Ong’s open source Python Materials Genomics (pymatgen) materials analysis library.

### Data Management and Open Access

A Superionic Conductor Database (SCDB) will be developed that will integrate all computed and experimental data arising from this DMREF. All experimental data generated will conform to typical data formats used widely in academia and industry.

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# High-Pressure Synthesis Directed by Theory

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**Keywords:** High-pressure, oxynitrides, photocatalysis, semiconductors for overall water splitting.

### Project Scope

High pressure (HP) offers access to chemistries not accessible at room pressure, and requires insights that limit the search space. We integrate theory and in situ synthesis to abbreviate the discovery cycle.

### Relevance to MGI

Efficiently closing the loop on prediction-synthesis-optimization-validation is conveniently provided by in situ synchrotron x-ray diffraction studies, which allow predictions of phase stability to be tested over a range of *p*T space for a single composition. Experimental results inspire modifications to the Universal Structure Prediction:Evolutionary Xtalography (USPEX) code that include lowered dimensionality and surface reconstruction to better predict phase stability.

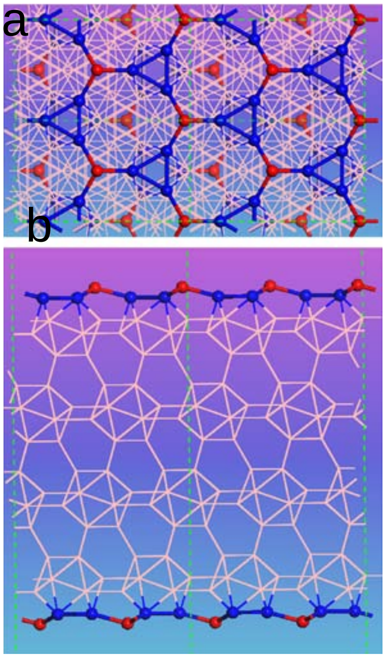

**Figure.** Reconstruction of the α-boron surface leading to increased stability: Projection of the 2 x 2 x 1 supercell **(a)** along the [111] and **(b)** [-1-12] directions. The inequivalent surface atoms are shown by different colors.

### Technical Progress

The success of large-scale industrial high pressure and thin film diamond synthesis inspires our search for and development of novel high value materials. Superhard materials, such as diamond itself, are often synthesized at HP. To discover new diamond-like carbon nets we combine theory to predict stability and reaction pathways with the novel reactive precursors that might allow access to them [1, 2]. We also seek efficiency semiconductors capable of overall water splitting under solar irradiation, and we target oxynitrides because of their stability and suitable band gaps. After harvesting predictions in the literature and limiting the compositional space using empirically derived guidelines, USPEX is used to predict structure, phase stability, band structure and properties [3-12]. In all cases tested so far, using $d^0/d^{10}$ and main group oxynitrides, no compounds are predicted to be stable at ambient conditions but are predicted to be stable at high pressure. Using *in situ* scattering we were able to verify that indeed the novel compositions predicted do only produce new phases at high pressure. The predicted structures and stability ranges were not correctly predicted. Specifically, theory predicts stability at higher pressures - >20 GPa rather than the experimentally observed 1 –5 GPa range, which is good news for possible large scale synthesis. The reasons for the discrepancy between theory and experiment include calculations carried out at absolute zero, neglecting the effects of order/disorder in the meal and O/N lattices and the possibility that the predicted phase is indeed stable at > 20 GPa and we have not accessed it experimentally. Further, our successful stabilization of HP phases at ambient pressures [13] was probably due to the added stabilization of surface reconstruction [14, 15], order/disorder or the effects of solid solution [16]. Surface reconstruction (Figure, [15]) on nanomaterials was a special focus of efforts to modify the USPEX code. Novel materials have been discovered experimentally at high pressure in the following systems coupled to GaN, and they have been characterized using combinations of in situ x-ray diffraction, neutron diffraction, diffuse reflectance spectroscopy and activity for overall water splitting: ZnO, $TiO_2$, $Nb_2O_5$, SrO, and CaO. The use of in situ scattering, carried out at Brookhaven and at Argonne National Laboratories is particularly valuable. An excellent example of this strategy is the synthesis of two novel phases in the GaN-$Nb_2O_5$ system at 1 GPa and 3 GPa with the rutile and $\alpha$-$PbO_2$ structures, respectively. In situ scattering identified these two phases, their structures, conditions of their optimal synthesis, that they were recoverable to room $p$.

### Future Plans

Although there have been great successes in correctly predicting and then synthesizing novel phases, including as part of this project [5, 17], correctly predicting the stability of the oxynitrides using USPEX has been challenging. Metastability [2] remains a powerful means of obtaining novel materials in large quantities. USPEX has been modified to include effects of surface reconstruction [6, 13] with variable surface stoichiometry [14] and variable overall composition [16] and was successfully tested in the search of relatively simple compositions [2-5, 7-12, 18]. It is clear from our experience with oxynitrides that the joint use of USPEX to predict properties and phase stability, and in situ x-ray scattering to determine optimal synthetic conditions is applicable to many other systems as well, including the areas of superconductivity [3, 8], mechanical strength [1, 4, 14], dielectrics [7, 9, 10] and hydrogen storage [18], for example.

Priorities going forward are to predict, characterize and utilize order-disorder as a band gap/edge tuning variable for overall water splitting. By way of motivation, we find that materials produced at high pressure and those produced using soft chemical routes [13] behave very differently under simulated solar irradiation; the high pressure produced materials are more robust toward corrosion and they are more active. Properties also depend on synthetic routes taken, as is to be expected for a metastable high-pressure phase produced at room pressure. We suspect that differences in band structure, probably due to vacancy ordering, anion ordering and surface reconstruction - or perhaps a combination of these effects - are responsible. USPEX will require further modification to cope with calculations that address these challenges, particularly with respect to order/disorder. The pay off is potentially great since mastery over these phenomena may allow us to take active phases produced only at high pressure and stabilize them - thereby providing cheap efficient routes to large volumes of material - using facile soft chemical routes.

### Broader impact (Optional for DOE grants/FWPs)

A data-rich era, less dependent on Edisonian approaches, where computational screening of target compositions based on their desirable properties is emerging. To match experimentation to widely used prediction tools, such as USPEX, it is critical to use *in situ* approaches and to allow students to appreciate both experimental and theoretical aspects of this endeavor. Amongst the fist of the USPEX workshops was held at Stony Brook in 2013 and allowed students to interact closely at the very beginning of this project; the most recent was held as part of the "100 years of crystallography" at the IUCr (International Union of Crystallography) meeting in August 2014 in Montreal Canada. These workshops consist of theory lectures, hands-on tutorial sessions, and round table discussions on the nature of the crystal structure prediction problems, how to address them, theory of energy landscapes, low-dimensional systems (clusters, surfaces) and experimental strategies to test theory.

### Data Management and Open Access

USPEX is continually updated and modified on the basis of experimental results and user feedback. USPEX_v9.3.9 is freely available at uspex.stonybrook.edu. Registered users can participate in the development of USPEX, in which case they become official coauthors of the code. Oganov, through forums such as workshops and social networks including USPEX GOOGLE GROUP, coordinates these activities.

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# New Energy Frontier Research Center: Center for the Computational Design of Functional Layered Materials (CCDM)

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**Keywords:** fundamental theory, defect engineering, multi-scale modeling, layered materials, catalysis

### Project Scope

The goal of the Center is to computationally design, synthesize, and experimentally characterize pristine and defected layered materials, such as $MoS_2$, for clean energy technologies such as solar cells, batteries, and catalysis of water splitting for the evolution of hydrogen fuel. Bulk materials, but also few- or single-layer systems, are of interest. An unusual feature of our Center is the development of improved wavefunction and density functional methods, including ways to treat the van der Waals (vdW) bonds that hold the layers together, and their implementation in computer codes. Success will be measured by the development and better understanding of new methods and materials.

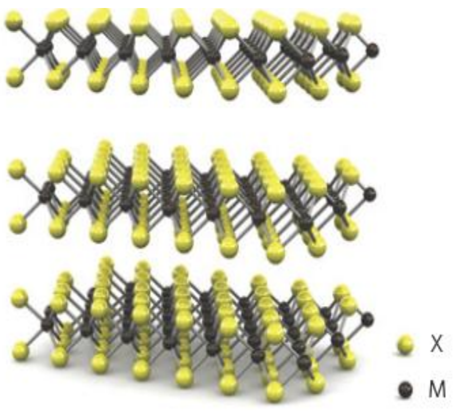

**Figure.** Structure of the layered transition metal dichalcogenide $MX_2$.

### Relevance to MGI

In our Center, there are three theoretical/computational thrusts (Thrust 1: methods development, Thrust 2: computational design, Thrust 3: multi-scale modeling), and two experimental thrusts (Thrust 4: synthesis and characterization, Thrust 5: catalysis). Each thrust has a monthly meeting, from which the Thrust Leader prepares a one-page written progress report. These reports are sent to all senior investigators, and are discussed in the monthly meeting of the Executive Committee (the Director and the five Thrust Leaders). The Executive Committee and the Scientific Administrator work to identify synergies and develop collaborations among and outside the thrusts, and in particular between theory/computation and experiment.

### Technical Progress

In Thrust 1, Weitao Yang and co-authors have investigated the particle-particle random phase approximation (pp-RPA) as an improved way to study excited states of many-electron systems. In the standard particle-hole (ph) RPA and its generalization in time-dependent density functional theory (TD-DFT), one finds the energies of particle-hole or neutral excitation as generalized eigenvalues of a Casida equation. In the pp-RPA, one finds the energies to add two electrons to the (N-2)-electron system in a similar way. In a study of binding energy curves for the molecule CH+, the pp-RPA gave accurate results while the TD-DFT predicted an excited state energetically below the ground state and missed a two-particle excited state completely. Also in Thrust 1, Gustavo

Scuseria and co-authors have investigated a pair coupled cluster doubles (pCCD) method that can treat strongly-correlated systems for which standard CCSD(T) fails, and a way to add back the weak correlations at CCSD(T) computational cost. In Thrust 2, Arun Bansil and co-authors have used density functional theory to predict the appearance of spin-orbit-driven topological-insulator (TI) and other phases in single- and few-layer systems, including (a) $MoS_2$, where a single layer displays strongly spin-polarized TI states, (b) silicene on Bi/Si(111), where the substrate destroys the TI phase but an electric field can restore it, (c) tin, where hydrogenation can destroy the TI phase in a single bilayer but restore it for two bi-layers, and (d) group IV and V transition metal bilayers in honeycomb structures, where in-plane strain can drive various electronic transitions. In Thrust 3, David Srolovitz, Jianwei Sun, and co-authors have used density functional theory with long-range van der Waals corrections to compute the energy landscape for translating one layer of graphene or BN with respect to another, or for changing the separation between layers. Computationally-inexpensive functionals were used to generate an analytic model for this energy landscape, which permitted the most accurate but most computationally-expensive method, the ph RPA in the adiabatic connection formula, to be used in a limited number of calculations to provide the few parameters needed by the model. In Thrust 5, Linyou Cao and co-authors have investigated experimentally how the degree of crystallinity and composition of $MoS_2$ affect three measures of its catalytic performance for hydrogen evolution; each measure is much more sensitive to crystallinity than to composition, suggesting ways to engineer this material for catalytic applications.

**Future Plans** (focus on on-going projects)

In Thrust 1, Scuseria's group will develop and implement density matrix embedding theory that will make it possible to carry out *ab initio* simulations of solid state materials using correlated-wavefunction methods. Perdew's group is developing a new computationally-efficient SCAN (strongly-constrained and appropriately normed) meta-generalized gradient approximation, which respects all known exact constraints including a strongly-tightened lower bound on the exchange energy, and may capture intermediate-range vdW interaction. This development is supported by NSF DMR (program officer Daryl Hess), but the functional will be applied to the layered materials in EFRC work. In Thrust 2, Ruzsinszky's group is benchmarking exfoliation energies of layered structures with different density functionals. Sun's group is computing point-defect formation energies in 2D materials. Wu's group has combined computations and experimental data to reveal the emergence of room-temperature ferroelectricity in ultra-thin films, challenging the longstanding notion that ferroelectricity is suppressed in thin films. In Thrust 3, Srolovitz's group plans to use their computed energy landscapes for layered materials as inputs to continuum elasticity models to investigate dislocations in bilayers. Haataja's group is improving the needed continuum elasticity models. Klein's group is building model systems to probe the mechanisms of catalysis on $MX_2$-type materials. In Thrust 4, the Xi and Iavarone groups are preparing a CVD growth of $MoS_2$ films. Iavarone's group will make STM characterizations of 2D chalcogenides. Zhu's group will make TEM studies of $MoS_2$, $TeSe_2$, and $NbSe_2$. Karapetrov's group is growing $TiSe_2$ and $NbSe_2$ single crystals, and optimizing the preparation of nanostructures by e-beam lithography. Borguet's group has started optical measurements on mechanically exfoliated $TiSe_2$, and will collaborate with members of Thrust 5 to investigate the microscopic details of water-splitting catalytic activity of birnessite. In Thrust 5, the Zdilla and Strongin groups are investigating water oxidation on the layered $MnO_2$ material birnessite. They find that oxygen evolution is increased by an order of magnitude when the surface is decorated with Mn(III). Cao's group is developing functional layered materials as high-performance electro/photocatalysts for hydrogen evolution in water. They suggest that few-layer $MoS_2$ nanoclusters with a lateral size of 5 to 30 nm provide a promising platform.

**Staffing Progress and Acknowledgments**

So far, the Center has hired 3 research assistant professors, 11 postdoctoral fellows, 15 graduate students, and 2 administrative staff members. Supported by DoE, Office of Science, Basic Energy Sciences, DE-SC0012575. (Program manager Craig Henderson).

# A Combined Experiment and Simulation Approach to the Design of New Bulk Metallic Glasses

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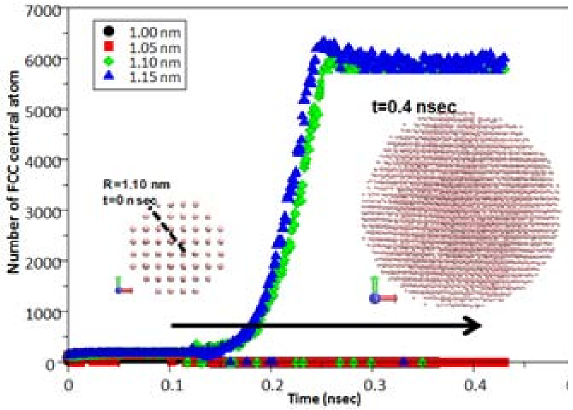
**Co-Principal Investigator, Izabela Szlufarska, Department of Materials Science and Engineering, University of Wisconsin-Madison, szlufarska@wisc.edu**
**Co-Principal Investigator, Paul M. Voyles, Department of Materials Science and Engineering, University of Wisconsin-Madison, voyles@wisc.edu.**

**Keywords:** Bulk Metallic Glass Design, Nucleation Kinetics, Glass Structure, Liquid Dynamics

### Project Scope

We propose that new insight into the contributions from alloying additions to stabilizing aluminum based metallic glasses can be gained from tightly coupled experiments on crystal nucleation and simulations on atom dynamics and transport from MD and cluster dynamic simulations starting from refined structures. The combination of experiments and simulations will be used to develop a new methodology for designing bulk metallic glasses, including a software package for structure determination combining accurate atomic interactions and measurements on short- and medium-range structure into a genetic algorithm refinement. New bulkier Al based metallic glasses will be designed and synthesized.



MD simulations from Szlufarska of Al at 600K, showing the number of atoms with a crystalline order as a function of time in a system with a crystalline nucleus in a supercooled liquid. The nucleus with initial radius of 1.10 nm grows while one with the initial radius of 1.05 nm dissolves. The critical nucleus size is estimated as 1.075 nm ± 0.25 nm.

### Relevance to MGI

In this initial phase of the project the coupling of experiment and simulation has progressed on two fronts. The MD simulations with accurate embedded atom method potentials have been able to reproduce the results from the analysis of nucleation measurements (thermodynamics and transport). A genetic algorithm optimizer is being developed to determine the optimal structure of an amorphous system given the simultaneous constraints of experimental and computed energy data. The optimizer is based upon a fitness function: Fitness = $\alpha\chi^2$ + E/atom, where $\chi^2$ is the error in the modeled vs. the true data, $\alpha$ is a weighting function, E/atom is the energy per atom, and Fitness is the total fitness of the structure being considered.. The tool has been tested on a crystalline nanoparticle and is being extended to amorphous structures.

### Technical Progress

For aluminum based glasses the kinetics that yields the extremely high product number density during primary crystallization is not well understood, Perepezko is developing a transient heterogeneous nucleation model informed by medium range order (MRO) information obtained through new FEM (Fluctuation Electron Microscopy) experiments that accounts for the nanocrystal size and density and satisfies thermodynamic and structural constraints . The goal of this work is to develop predictive capabilities within the Al-based glasses as well as a generic framework for other MRO mediated precipitation reactions. Doping 1 at.% of Cu to the Al-Y-Fe glasses changes the crystallization onset, $T_x$ dramatically. The replacement of Al by Cu results in an 11°C increase of $T_x$ and increases the delay time by a factor of ten. However, the substitution of Y by Cu leads to a 40°C decrease of $T_x$ with no delay time. Clearly, the Cu substitution has a large effect on atomic transport. The understanding of MRO catalyzed crystallization is critical to developing strategies to control it in order to enhance glass formation and to achieve bulk amorphous material.

Voyles and Morgan have worked with postdoc Min Yu to develop an integrated genetic algorithm optimization tool called StructOpt that can determine complex atomic structure by matching forward modeling to experimental data and simultaneously minimizing the energy. This tool integrates the power of GAs for complex optimization and utilizes both available experimental and energy data simultaneously. We have tested the first version on Au nanoparticles using scanning transmission electron microscopy (STEM) data and an embedded atom method potential and found excellent ability to identify experimental structures up to 5000 atoms. We are now developing the tool for application to amorphous structures.

Voyles and Perepezko have used an existing hybrid reverse Monte-Carlo (HRMC) structural refinement tool to study the structure of $Ni_{60}Nb_{40}$ metallic glass amorphized both by rapid quenching and by intense deformation. Although the two glasses are indistinguishable in x-ray and electron diffraction, FEM data show substantial differences, which HRMC modeling reveals to be structural memory of the bcc crystal structure of the Nb in the deformation-induced glass. The two glasses have different crystallization behavior in calorimetry; further simulations based on refined structures may reveal the connection to the atomic structure in the glass state.

## Future Plans

The StructOpt code will be integrated with FEM and x-ray structure factor data to identify amorphous structures in the metallic glasses under study. The code will be documented and released.

We will use coupled experiments and simulations to understand the atomic structure and dynamics underlying glass-formation and crystal nucleation as a function of composition in $Al_xLa_{100-x}$ metallic glasses. La-rich compositions form bulk glasses, while Al-rich glass do not. We will synthesize glasses, then measure their thermal characterization, nucleation behavior, and structure. Structure data will be used to refine atomic models, which will be used as the starting point for simulations to connect aspects of structure to glassy dynamics and crystal nucleation. Based on those connections, we will test minor additions to the Al-rich compositions to find additions that mimic the structure and dynamics characteristic of bulk glasses, first in simulations, then in experiment. Further structure determination and simulations will close the design loop, leading to bulkier Al-based glasses.

## Broader impact

The StructOpt code being developed in this study is being made user friendly and publically available to support broad impact cyberinfrastucture. StructOpt is available under open source licensing as part of the MAterials Simulation Toolkit (MAST), and can be obtained from https://pypi.python.org/pypi/MAST. An undergraduate student from UW-Madison participated in the process by developing FEM data analysis software for release to the broader community of scientists as both a software tool and online application on the MaterialHub (materialshub.org). That software has been adopted by researchers at the University of Muenster and the Bhabha Atomic Research Center.

## Data Management and Open Access

FEM data sets for various MGs and data analysis software have been posted at http://tem.msae.wisc.edu/papers.

## Publications

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# The Materials Project: Merging Ab Initio Calculations, Supercomputing, and Data Science for Materials Genomics

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density functional theory, high-throughput computations, li ion batteries, data mining, materials informatics

## Abstract

The Materials Project (www.materialsproject.org) – part of the broader Materials Genome Initiative - is an effort to compute the properties of all known inorganic materials and beyond, and offer that data to the community together with online analysis and design algorithms.[1] The current release contains data derived from density functional theory (DFT) calculations for over 60,000 materials, each with searchable associated properties such as relaxed structure, electronic state, energy storage capability, aqueous and solid stability, and more. Furthermore, software algorithms are offered by the Materials Project and can be used by researchers for materials informatics, including both interactive web-based tools like the Phase Diagram App and the Pourbaix App, as well as open-source codebases and data access tools such as the pymatgen materials analysis library,[2] FireWorks workflow software,[3] and Materials API.  This presentation discusses the development of the Materials Project and its growth attracting >10,000 registered users. The application of the infrastructure and data to several materials design problems, including advanced batteries and thermoelectrics, along with usage in diverse fields of study by external users will be presented. Lastly, we will cover up-and-coming features and developments, such as calculation of the largest data set of elastic tensors, additional band structure-derived properties, user-submitted structures for computations, and integration with outside projects such as the Nanoporous Materials Genome Initiative.

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[3] http://pythonhosted.org/FireWorks/

# Programmable peptide-based hybrid materials

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**Keywords:** Biomaterials, peptides, proteins, bionano, self-assembly

### Project Scope

Given nature's ability to encode structure, functionality, and self-assembly into amino acid sequences, peptides and proteins offer tremendous potential in the design of new materials that can efficiently and economically address many current limitations in the creation of biomolecular materials. Using a close interplay between theory, computational design, and experiment, we are developing approaches for biomaterials design that will enable a priori prediction of sequences to yield a target nanostructures and assemblies.

### Relevance to MGI

Leveraging concepts from statistical mechanics, computational methods are being developed to design amino acid sequences compatible with predetermined crystalline ordering in (2-D) lamellar sheets with nano-crystalline order. Candidate (poly)peptides are being synthesized and characterized. New solution assembly methods employ kinetic control and hierarchical, multistep and multicomponent processes to build these materials. Cryogenic transmission electron microscopy tomography (in addition to the use of scattering, microscopy and spectroscopy techniques) are being developed an applied to characterize the resulting structures as they assemble. The relative importance of intermolecular interactions are being assessed by these experimental studies and incorporated into the computational methods.

### Technical Progress

The project has produced the first versions of theoretically predicted peptide sequences for targeted 2-D nanostructure solution assembly. Helical peptides were designed to assemble into tetrameric proteins with a hydrophobic core and external residues, whose amino acids can be designed to foster a targeted inter-bundle assembly. The theoretically predicted sequence was subsequently synthesized. Importantly, the circular dichroism clearly shows the sequences produce helical conformations, and the proteins retain these helical structures over a wide range of temperatures (20-70 C). Initial solution assembly of one sequence produced the platelet nanostructure shown in the cryogenic transmission electron microscopy image (Figure). The observed rectangular platelets are consistent with the successful assembly of the targeted 2-D lattice (P222 space group). These data strongly support the theory-driven materials design. The results also highlight the need for further study of the kinetics of assembly to produce more regular, assembled materials as well as to study new predicted sequences.

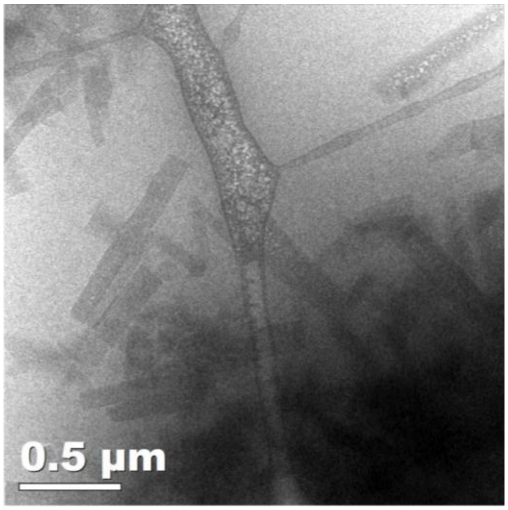

**Figure.** Cryogenic transmission electron microscopy of theoretically designed peptide sequence showing clear inter-bundle platelet assembly.

## Future Plans

Via iterations of computational design, synthesis, and experimental characterization of nanostructures, we will explore a wide variety of features and properties in the design and stabilization of peptide nanostructures. These include: (a) the tailoring of noncovalent and covalent interactions to foster structure formation via self-assembly and its stability via chemical cross links, (b) the development of methods for processing these peptide materials and their structural characterization of the nanostructured assemblies via electron microscopy and x-ray/neutron scattering, (c) leveraging the knowledge gained to arrive at a variety of nanostructures that allow positioning of chemical groups and metal or metal oxide nanostructures and the development of new bio-nano hybrid materials.

## Broader impact (Optional for DOE grants/FWPs)

Graduate students and postdoctoral researchers from a variety of natural science and engineering backgrounds are learning state of the art theory, synthesis, and materials engineering methods. The project requires the close interplay of computational design and modeling with synthesis and experimental characterization.

## Data Management and Open Access

Computer codes are currently under development but are being structured so as to facilitate their use in a wide variety of potential applications. Data is being collected, annotated, and stored in manner suitable for use by a variety of researchers.

## Publications

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# Discovery, Development and Deployment of High Temperature Coating – Substrate Systems

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**Keywords:** alloy design, multilayers, superlattice intrinsic stacking faults, Co-Al-W

## Project Scope

The goal of this project is to develop new computational and experimental approaches that accelerate the design of multilayered systems for extreme high temperature thermomechanical environments. Multicomponent, multiphase substrates based on the emerging Co-Al-W system are a primary focus, due to their exceptional high temperature mechanical properties. New computational tools deployed include (1) a self-consistent framework for alloy design that rigorously couples first principles calculations and multicomponent thermodynamics, (2) a high throughput thermomechanical code for exploration of the design space for multilayers and (3) a particle-based dynamic code parallelized with GPUs that addresses the challenging problem of designing failure resistant interfaces. These computational codes have guided the experimental program, which has identified new high strength alloy compositions and robust coatings.

## Relevance to MGI

To narrow the design space for expensive and time consuming single crystal growth and mechanical property experiments, the first principles-based alloy design framework has been employed to design several generations of high strength substrate alloys. For design of the protective outer layers, a high throughput code for thermomechanical performance has been employed for selection of intermetallic coatings for experimental investigations and to assess the challenges for ceramic thermal barrier layers. The particle-based dynamic GPU code has guided the design of a new femtosecond laser-based technique for measurement of interfacial toughness.

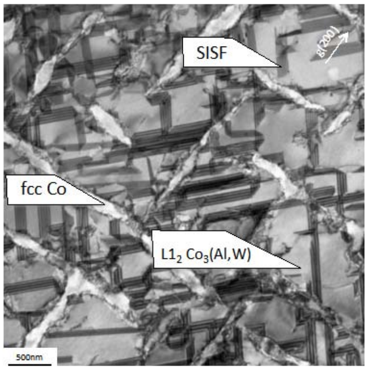

**Figure 1 –** A two phase fcc-Co + L12 $Co_3(Al,W)$ alloy Co-6.7Al-8.1W-6.2Ti (at%) after 2% deformation at 900°C showing a high density of SISFs in the $L1_2$ precipitates.

## Technical Progress

Fundamental requirements for robust high temperature multilayered systems include a substrate with high resistance of the to plastic deformation beyond 75% of the melting temperature and multiple outer layers with good adherence that provide resistance to aggressive chemical and thermal environments. Substrates comprised of fcc-Co strengthened with the $Co_3(Al,W)$ intermetallic $L1_2$ phase (only recently discovered in the Co-Al-W system) have been a major focus. Electron microscopy studies have revealed very unusual modes of deformation that involve the formation of superlattice intrinsic stacking faults (SISFs), Fig. 1, formed as a result of $L1_2$ precipitate shearing. Recent HAADF-STEM studies also reveal compositional fluctuations in the vicinity of these faults, Fig. 2. We therefore hypothesized that alloys with high SISF energy and low tendency for segregation would possess the most promising properties. Since it is impossible to measure the SISF energy experimentally, we employed a combination of first principles techniques based on density functional theory and a statistical mechanics infrastructure to (1) guide the design of new compositions with high SISFs, (2) address fundamental issues of the stability of the $L1_2$ phase at finite temperatures and (3) assess the driving forces for chemical segregation at the SISFs. The ternary Co-Al-W 0K phase diagram has been calculated; the $L1_2$ phase is not stable at this temperature, however, accounting for vibrational and configurational entropy, the $L1_2$ phase is stable above 600°C. First-principles calculations also indicate that additions of Ti, Ta, Nb and Hf stabilize the $L1_2$ phase and increase SISF energy. Single crystals of alloys containing Ti, Ta and Nb fabricated experimentally via the Bridgman technique indeed have high solvus temperatures and exceptional high temperature strength. Fluctuations in Al, Ta and W at SISFs observed experimentally could substantially alter fault energies, Fig. 2 and therefore strongly affect strength.

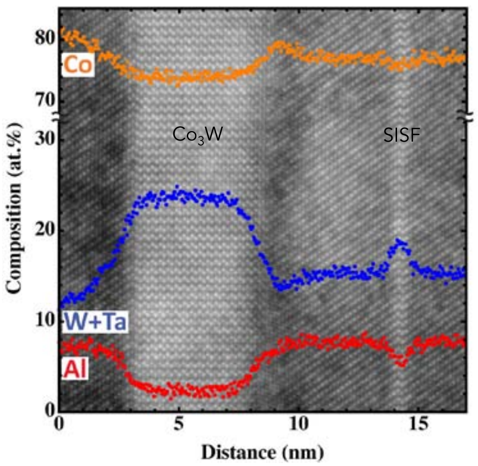

**Figure 2 –** A HAADF-STEM image of a three phase fcc-Co + $L1_2$ + $DO_{19}$ Ta-containing alloy showing an enrichment of W and Ta and depletion of Al at the SISF (which has local $DO_{19}$ atomic stacking). First principles calculations of the SISF energy demonstrate that these fluctuations substantially lower the fault energy for this alloy.

The load-bearing metallic substrate typically requires an intermediate intermetallic layer for chemical protection and an outer ceramic layer for thermal protection. Again, the design space is immense, the layers will have disparate properties and techniques for assessing interfacial properties are lacking. A high throughput code for assessment of the thermomechanical performance of multilayers has been developed. Given the properties of the Co-substrate, relatively thin coatings are likely to be required to minimize the driving forces for cracking at the intermetallic and ceramic interfaces. A new dynamic particle-based code that can assess competing failure modes within multilayered systems has been developed with GPU parallelization; the performance enhancement of over multi-core CPUs is a factor of about 300 (per CPU core). This code is being used to establish layer failure mechanism maps and to tune the conditions by which femtosecond laser pulses are deposited to detach films for measurement of the toughness of the interface.

## Future Plans

Continued development of the alloy design computational infrastructure and application to higher order multicomponent systems over a broader set of property space. Further development of particle-based approaches for insights to precipitate-scale plastic processes. Combinatorial experiments on oxide formation using ion plasma deposition facilities at GE and measurements of interfacial toughness of oxide-metal interfaces.

## Broader impacts

There have been several student research exchanges between UCSB and the Univ of Erlangen and the Ruhr Univ of Bochum. UCSB has hosted two summer schools, on 3D Materials Science (2013) and Integrated Computational Materials Science & Engineering (2014). Students attended DMREF workshops that were held at GE Global Research in 2013 and 2014.

## Data Management and Open Access

The high throughput multilayer code is programmed in Mathematica and will be available for all platforms as a part of a textbook being authored by Begley. The first principles and statistical mechanics alloy design code will be open source and available at GitHub. Thermodynamic data generated in the program is now available in the Computherm Co alloy database. The more specialized particle-based GPU codes remain under development. All other experimental data has been or will be published in archival journals.

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# Center for Accelerating Materials Modeling (CAMM) from SNS Data.

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**Keywords:** neutron scattering, refinement of force fields, molecular dynamics

### Project Scope

Neutron scattering enables simultaneous measurement of structural and dynamic properties of materials from the atomic scale (0.1 nm, 0.1ps) to the meso scale (1um, 1us). These ranges are remarkably complementary to current capabilities of computational modeling and the simplicity of the scattering cross section allows the prediction of neutron scattering data relatively straightforwardly from atomic trajectories in a computer model. As such, our goal is to accelerate the rate of scientific discovery through the integration of materials modeling and simulation into all aspects of the neutron scattering experimental chain. This enables refinement of model parameters such as force fields and allows researchers to compare model and experimental results in near real time. These advances will facilitate our ability to perform validated materials modeling to achieve capabilities for materials by design. Our science focus is *to understand the mesoscopic dynamics and transport in crystalline and non-crystalline materials that underpin diffusive phenomena of single particle properties such as mass, proton, and ion transport that are facilitated by collective motions.*

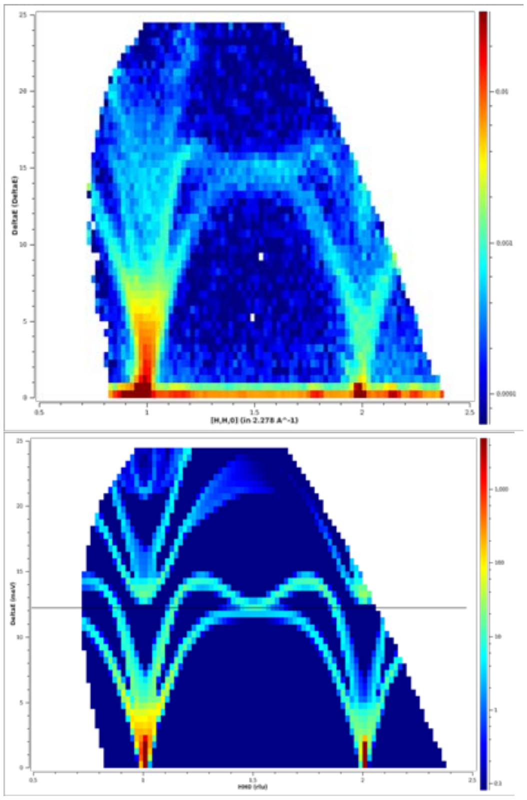

**Figure.** Top panel shows neutron scattering S(Q,E) of $SrTiO_3$ measured on HYSPEC at the Spallation Neutron Source. Bottom panel shows ab-initio molecular dynamics simulation results obtained in real-time during the experiment.

### Relevance to MGI

The ability to correlate the atomic, nano- and mesoscale-structure with physical properties (e.g., mechanical, chemical, electrical) and functionality is critical to the rational design of the next generation of energy materials. Neutron Scattering provides unique insight into the structure and dynamics of over a wide range of important length and time scales and it does so materials in a fashion that does not substantially damage or modify the materials. CAMM is providing model parameter refinement tools based on neutron data as well as real time materials simulation capabilities enabled through leadership computing and advanced data analytics. This capability enables improving the predictive capability of materials models based on validation with neutron data as well as facilitating planning for targeted neutron scattering experiments based on model predictions (e.g., theory/simulation guided experiments).

## Technical Progress

The Center for Accelerating Materials Modeling (CAMM) began with the goal to drive the science-based development of software tools to link neutron scattering and computer modeling. In this regard, we have developed a refinement loop using classical molecular dynamics (MD) as the modeling technique, in combination with quasielastic neutron scattering data from the BASIS instrument. We have successfully demonstrated the refinement of MD force-field parameters for LiCl, and the software capabilities developed have been subsequently used in several projects initiated by SNS users. The software tools and capabilities developed to enable these studies are broadly made available to SNS users. Other successful studies are highlighted by recent work on $VO_2$ in collaboration with J. Budai and O. Delaire. In this case, we investigated the thermodynamic forces driving the metal-to-insulator transition in $VO_2$, and showed for the first time that the metallic phase is stabilized by a large phonon entropy. In a related effort, we were able to accurately account for the effects of anharmonicity on the phonons in SnTe and PbTe thermoelectrics, using inelastic neutron scattering and ab-initio MD simulations at finite temperature. Finally, as part of the efforts to integrate modeling and neutron scattering experiments in ‘real time’, a pilot experiment was carried out that enabled instant access to high performance computing during an experiment on the HYSPEC instrument. This allowed the team to carry out ab-initio molecular dynamics simulations and to use the results for decision making during the actual experiment, maximizing scientific output from the neutron beamtime.. As part of outreach to SNS users and the broader scientific community, the current version of CAMM developed tools and the refinement framework has been made available including documentation, tutorials located at the website http://camm.ornl.gov.

## Future Plans

Based on the demonstrated ability to perform force-field refinements from neutron data (e.g., experimental validated computational models), CAMM will focus on using this capability toward developing fundamental understanding of dynamics and transport in non-crystalline materials such as polymers, gels, composites, or glasses. Such materials challenge many models/simulations due to intrinsically possessing numerous metastable or non-equilibrium states, length scale dependent collective and heterogeneous dynamics, strong interplay between entropic and enthalpic effects, morphologies that evolve during transport, and geometric confinement effects in thin films. Yet these materials have very broad potential for applications in various energy related technologies, including light-weight materials, chemical separations and purification, energy conversion and storage. One aspect that is clear, is that the dynamics (i.e., molecular motions) are key to many of the most important macroscopic properties (including transport within and through the materials); yet our understanding of dynamics, especially at the mesoscale (between the atomic/molecular scale <0.5-1 nm and continuum limit >30-100 nm), remains extremely limited. In this regime, the dynamics typically involve collective motion, which are ideally studied using neutron scattering, augmented with validated molecular modeling/simulation. Additionally, the intrinsic coupling between materials static and dynamical behavior makes neutron scattering (elastic and inelastic) an ideal approach for elucidating the fundamental relationships to macroscopic properties. Thus, our overarching goal is to understand the mesoscopic dynamics and transport in non-crystalline materials that underpins diffusive phenomena of single particle properties such as mass, proton, and ion transport that are facilitated by collective motions. This future focus will also serve as a resource to bridge gaps/needs in other MGI-related projects and to a broad class of neutron users.

## Data Management and Open Access

Documentation, tutorials and codes related to the CAMM refinement workflow are publically accessible through the website http://camm.ornl.gov. Users of the SNS and HFIR facilities have access to the facilities analysis infrastructure which has the CAMM framework installed. CAMM is also working closely with the Compute and Data Environment for Science (CADES) project at Oak Ridge National Laboratory to provide data access and citation in the future.

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# High-Throughput Mapping of Functional Dielectric-Metallic Heterostructures

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**Keywords:** perovskite oxide superlattices, electronic properties, off-axis sputter deposition, density functional theory, interface effects

## Project Scope

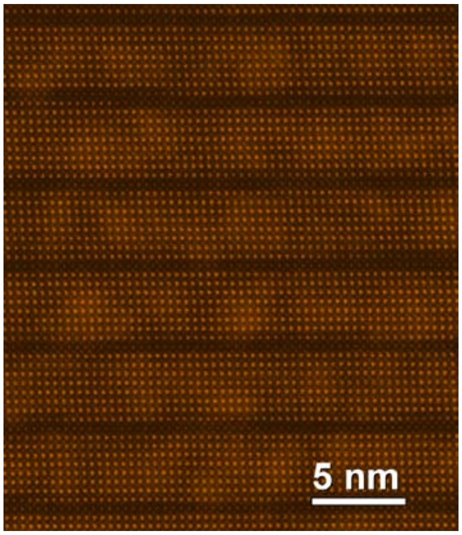
The principal objective is to map the structure and properties of three selected broad families of metallic-dielectric perovskite superlattices through an integrated theoretical-experimental approach. This combines first-principles calculations, construction of first-principles-based models, development of a guided-sampling high-throughput first-principles approach, and experimental synthesis and characterization of selected systems. Success is measured by the identification, synthesis and characterization of individual systems with targeted functional properties or unusual and distinctive behavior that validate the map and will potentially be suitable for technological applications.

## Relevance to MGI

The team includes all the necessary capabilities for first-principles computation, modeling, synthesis and characterization of metallic-dielectric perovskite oxide superlattices, with a long track record of previous collaboration. The models are tested both for their ability to reproduce first-principles data and for their ability to predict and interpret the results of experiments. Dawber's enhanced thin film growth capabilities allow growth of superlattices specifically selected to test model predictions, allowing iterative improvement of the models as needed; one example of this iteration in the current project is the synthesis of specific $PbTiO_3/BaTiO_3$ superlattices predicted by the model to have the highest piezoelectric coefficients.

## Technical Progress

Enhancement of piezoelectricity in $PbTiO_3/BaTiO_3$ superlattices has been established through first-principles calculations. Interface effects have been identified as the origin of the enhancement, supported by analysis of atomic positions obtained from first-principles calculations. Experimental synthesis and characterization of specific superlattices predicted to have the highest piezoelectric response is in progress, and will be used to validate and refine the model. Parallel analysis of the piezoelectric response in related superlattices, including $BaTiO_3/CaTiO_3$, is underway.



*HR-STEM image of a $PbTiO_3/SrRuO_3$ superlattice grown in Dawber's laboratory.*

$PbTiO_3/SrRuO_3$ superlattices [1] are the prototypical metallic-dielectric superlattice for this project, and integrated experimental-theoretical investigation has yielded new insights. Experimentally, it has been found that significantly higher dielectric responses can be achieved in $PbTiO_3/SrRuO_3$ superlattices when symmetric top and bottom $SrRuO_3$ electrodes are deposited in situ. We have also seen evidence for tunneling currents between adjacent metallic layers through the ferroelectric layers. On the theoretical side, SBU graduate student Simon Divilov and Fernandez-Serra have performed DFT studies indicating that the oxygen vacancies are most likely charged and reside in the SrO layers; these features have been incorporated into the phenomenological description of these systems. More generally, Fernandez-Serra, Divilov and Chandra are developing a dynamical model to distinguish extrinsic (e.g. O vacancies) and intrinsic (e.g. inversion-breaking interfaces) contributions to self-poling, with predictions for temperature and frequency dependent measurements to be tested by Dawber and Du.

Important experimental and theoretical capabilities needed for the project have been developed. A new deposition system, designed and assembled by Dawber, is near completion. An efficient method for first-principles determination of superlattice structures has been developed and tested for familiar ferroelectric-dielectric superlattices, and is available to the community on a website [2]. The first application of this "stacking method" to metallic-dielectric superlattices has been incorporated into a pilot study of $SrCrO_3/SrTiO_3$ by Zhou and Rabe. First principles calculations to build the necessary database of low-energy structures of the constituent compounds for the superlattice families of interest to this project are underway, with results obtained to date for $SrTiO_3$, $SrCrO_3$ and $SrCoO_3$.

### Future Plans

The activities on $PbTiO_3/BaTiO_3$ and $PbTiO_3/SrRuO_3$ will continue, with a focus on connecting theoretical and experimental results. We will complete the design of the constituent compounds database, adding information for more compounds, and work on the development of first principles models to capture the metallic vs dielectric character of a given superlattice. We will then refine the models to make quantitative predictions of band gaps and features of the bandstructure and phonons relevant to thermoelectric performance. We will begin the growth and characterization of new material combinations in the new deposition system. The first systems to be grown, which have been highlighted as interesting by theory, will be $SrCrO_3/SrTiO_3$ and $SrCoO_3/SrTiO_3$.

### Broader impact

Three theoretical graduate students, Simon Divilov (SBU), Yuanjun Zhou and John Bonini (Rutgers), have been collaborating in the development of the necessary methods and work on the constituent compound database. At SBU, in the past year the project has supported a full-time experimental PhD student, Greg Hsing, and an experimental summer student, Rui Liu. A high school student, Saranesh Prembabu, carried out research in the Dawber lab as part of the Simons Summer Research Program.

### Data Management and Open Access

The superlattice structure determination scripts have been made available to the community on a website constructed by Zhou [2]. Bonini is working with emerging software tools for storing and accessing results of first-principles calculations (AflowLib, Materials Project and AIIDA), to design our constituent-compounds database as an overlay. This will allow us to share the first-principles results with other users of the software and will provide a prototype for constructing special-purpose databases that are widely accessible.

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**Publications**

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2. P. Chandra, P. Coleman and R. Flint, *Ising quasiparticles and hidden order in* $URu_2Si_2$, Philosophical Magazine **94**, 3803 (2014).

# Search for Magneto-electronic Behavior in Complex Fluoride-based Interfaces

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**Keywords:** multiferroics, fluorides, ferroelectrics, interface based device, density functional theory

## Project Scope

The project will consist of a systematic study of the magnetoelectric properties of fluoride perovskites and fluoride/oxide interfaces. While in oxide perovskites ($ABO_3$) ferroelectricity is driven by the displacement of the B-element, fluoride perovskites are mostly A-element driven. Therefore, new phenomena should appear in fluoride-based materials and interfaces. Adding other degrees of freedom, such as magnetic cations, lattice strain and spin-orbit coupling, could offer a large variety of new physics to be explored. Success will be measured by the discovery of fluoride-based magnetoelectric materials.

## Relevance to MGI

This project relies on strong theory/experiment collaboration, where theory will characterize fluoride materials and fluoride/oxide interfaces using DFT, while experiment will synthetize and characterize the most promising ones. Experimental results will be used to improve the theoretical approach. For example, theory has predicted a magneto-electric effect in $NaMnF_3$ and the experimentalists are synthesizing epitaxial thin films of this material on $SrTiO_3$ substrates to corroborate the theoretical prediction. Computation of fluoride/oxide interfaces also is currently under way (Fig. 1).

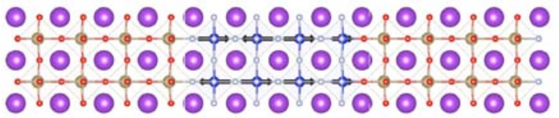

**Figure 1.** Magnetic moment configuration at the multilayer $KTaO_3$/$KNiF_3$. Note the ferromagnetic alignment at the interface.

## Technical Progress

We have found that $NaMnF_3$ has a ferromagnetic response, as shown in Fig. 2. Our computational results indicate that the material should be a strong weak ferromagnet. Thin film samples have been grown via molecular beam epitaxy along the [100] axis. Magnetic measurements seem to confirm the existence of a magnetic/weak ferromagnetic phase below a temperature of approximately 68 K. We are now in the process of measuring the ferroelectric and magnetoelectric properties as a function of temperature. Our initial measurements using lateral electrical contacts were challenging because of the large dielectric constant of the $SrTiO_3$ substrate. We are now growing samples on Nb-doped $SrTiO_3$ to measure the ferroelectric and magnetoelectric properties in a vertical geometry. We are also studying computationally different interfaces, and in particular we have detected that in $KNiF_3$/$KTaO_3$, both antiferromagnets, the system tends to be ferromagnetic at the interface (Fig. 1). We are in the process of validating our results by varying the localization parameter in the DFT+U description.

In addition, the multiferroic fluoride $BaCoF_4$ has been successfully grown in thin film forms on $Al_2O_3$ (0001) substrates by molecular beam epitaxy. These transparent films have orthorhombic structures with the long orthorhombic axis out-of-plane, and three in-plane twin domains at $120^{o}$ from each other. The ferroelectric phase is observed up to room temperature with the easy axis in-plane. Magnetic measurements show the expected bulk antiferromagnetic behavior below 75 K and two additional transitions at $T_{C1}$=17 K and $T_{C2}$=41 K yet to be identified. To interpret the experimental observations, DFT calculations are being performed to analyze the effect of *ac*-plane epitaxial strain. Preliminary results reveal a non-linear coupling between the polarization and the epitaxial strain with an enhancement of the spontaneous polarization for positive values of strain (i.e. expansion). These findings provide a new, promising route for synthesis of new multiferroic materials.

## Future Plans

We will proceed with an exhaustive search for enhanced and/or new *ferroelectricity and multiferroicity/magnetoelectricity in fluoride-based interfaces*. For this purpose, and based on our preliminary results, three interfaces are being studied: NaMnF$_3$/LiMnF$_3$, NaMnF$_3$/SrTiO$_3$ and NaMnF$_3$/BaCoF$_4$. In particular, we are interested in systems where the interface manifests properties which are different than those of the pristine materials. For example, for the proposed interfaces we expect that geometrical and improper ferroelectricity coupled to magnetic ordering should occur, creating new electronic states that can be measured. As a second and even more ambitious goal we propose *the coupling of electronic properties: 2DEG, magnetic ordering, ferroelectric switching and Rashba splitting in fluoride-based interfaces and superlattices* by tuning the multiferroic magnetoelectric properties with a particular spin-texture at the interface. Here, KTaO$_3$/Na$M$F$_3$/BaCoF$_4$, and BaCoF$_4$/SrHfO$_3$ superlattices and interfaces will theoretically studied, and if our preliminary results are corroborated, experimental efforts will be addressed for their synthesis.

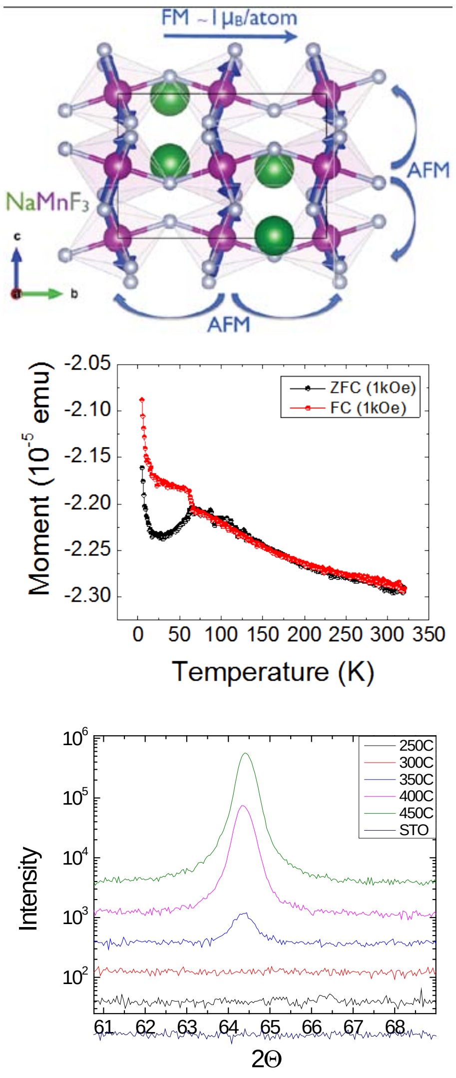

**Figure 2.** Bottom: x-ray diffraction of various NaMnF$_3$ films (30 nm thick) showing the (400) reflection. Middle: magnetization measurements of the films, indicating the strong magnetic properties, possibly as a result of weak ferromagnetism. Top: results of DFT calculations indicating the origin of weak ferromagnetism in this compound.

Until now, we have been able to clarify the role of the A-cation in fluorides, where we have demonstrated that phonon driven ferroelectricity is mostly coming from this cation. Therefore, this adds the possibility of including a magnetic B-cation, which could lead to a strong magneto-electric response. Along these lines, we have focused on NaMnF$_3$, where we have theoretically demonstrated the existence of the magneto-electric coupling even with very small stress. Experiments are being performed to test this result. Additionally, our preliminary results on KNiF$_3$/KTaO$_3$ demonstrate that even though the pristine materials are antiferromagnets, the system behaves ferromagnetically at the interface. This indicates that this type of materials should manifest exchange-bias.

## Broader impact (Optional for DOE grants/FWPs)

In order to perform the proposed goals, three postdocs, each to work for each investigator, as well as two graduate students are going to be involved in the research. These students and postdocs will be trained in state of the art computational and experimental skills, including DFT calculations and materials growth and characterization techniques. Joint group meetings between all participants will enhance the appreciation of the synergy of having computational and experimental skills in order to perform efficient materials research projects.

## Data Management and Open Access

A software to perform analysis of spin structure and detailed analysis of electronic bands as obtained from the Ab initio code VASP has been created and it will be made public in the next few months. Additionally, a code for general purpose generation of interfaces will be also created and made public before the end of the project.

# Discovery and Development of Additives for Novel Polymer Morphology and Performance

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**Keywords:** Polyolefins, nucleation, additives, crystallization, semicrystalline polymer morphology

### Project Scope

The goal of the project is to prototype a new paradigm for the development and design of additives that significantly affect the nucleation and growth of polymer crystallites, the evolution of novel morphologies as a consequence of new crystallization behavior, and the engineering of polymer material properties through the modification of semicrystalline morphology. Molecular simulations are performed to assess the effects of various additives on nucleation and growth of oligo-ethylene. Rheometry, differential scanning calorimetry, small angle light scattering, and neutron scattering are employed to measure indirectly the early onset and ultimate morphologies of selected additives.

### Relevance to MGI

Direct observation of nucleation events, crystal growth mechanisms and the resulting molecular scale organization in semicrystalline polymers remains a challenge for traditional experiments. We employ molecular simulations to perform experiments *in silico*, thereby revealing the molecular nature of nucleation and growth in the presence of additives. Simulation results guide the choice of additives for experimental study. The observed macroscopic morphologies are then related back to the molecular crystallization rates using a kinetic model. In this manner, an iterative process of simulation and experimental validation and evaluation is used to explain the behavior of existing additives and to discover new ones.

### Technical Progress

Molecular simulations are performed using the LAMMPS package. In addition, we have developed a suite of software routines to build and analyze simulation results for heterogeneous systems comprising polymer and nucleating agent. The protocols have been validated using crystal growth for n-pentacontane (C50), which is believed to proceed via a surface nucleation mechanism, as the case study. These simulations are illustrated in Figure 1. Simulation data for the propagation of the C50 crystal growth front from the [110] surface of crystalline polyethylene into the bulk C50 melt have been analyzed for growth rates and surface nucleation events. Analysis of mean first passage times has been employed to measure surface nucleation rates on each layer of the propagating C50 crystal, as well as the subsequent lateral spreading rate within each layer following nucleation. The mechanism of growth is interpreted in terms of the surface nucleation and spreading rates, and comparison is made to the classical regime theory of Lauritzen and Hoffman [1].

Currently, we are simulating melts of C50 with a number of foreign surfaces based on the Stillinger-Weber (SW) potential to represent the family of tetrahedrally-bonded crystals that includes silicon, germanium and diamond. By scanning the SW parameter space, we can systematically examine the entire family of these materials, including not only the real materials but also hypothetical ones, in order to establish trends in effectiveness as nucleating agents. We are also examining the different crystal facets within this family of nucleating agents. Evaluation of nucleation effectiveness is performed using the protocols previously validated for C50 on polyethylene.

Experimental efforts to date have been devoted to dispersing nanoparticles in non-polar polyolefins. This is necessary to realize the full potential of such additives to enhance the thermo-mechanical properties of polyolefin nanocomposites. To this end, methods have been developed to attach polyolefin chains onto the nanoparticle

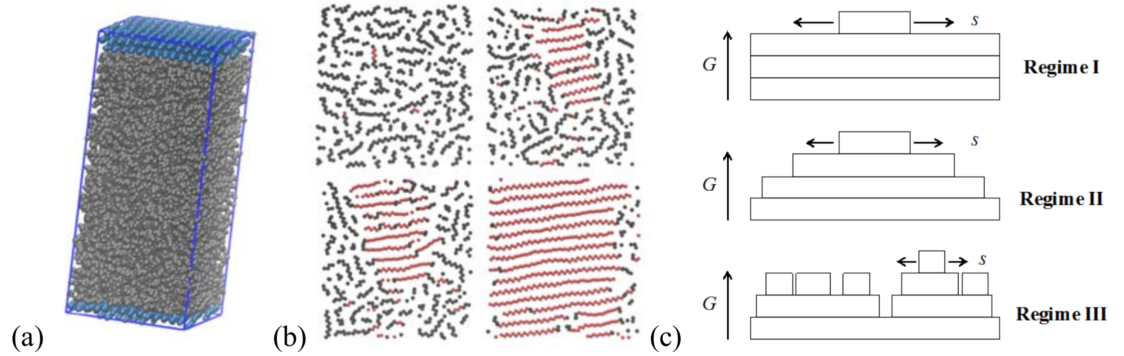

Figure 1. (a) Image of simulation cell, comprising a C50 melt between two crystalline surfaces. (b) Snapshots from a simulation at 360K illustrating nucleation and spreading of crystalline C50 (red sites) from molten C50 (black sites) within a 0.4 nm layer at the crystal growth front; time sequence proceeds in reading order from upper left to lower right. (c) Illustration of crystal growth front propagation (*G*) as a consequence of surface nucleation (*i*) and spreading (*s*) kinetics, according to Regime Theory.

nanoparticles (PE-g-$SiO_2$) with grafting densities from 0.10 to 0.35 chains/$nm^2$. The resulting PE-g-$SiO_2$ was blended with linear low density poly(ethylene-co-hexene) (LLDPE) with nanoparticle concentrations varying from 2 to 6 wt% silica. The LLDPE blends were analyzed by melt rheology, neutron scattering, thermal studies of crystallization and melting, and solid-state microscopy. At 2 wt% loading of PE-g-$SiO_2$, atomic force microscopy revealed small clusters of 3-7 nanoparticles, as well as singly dispersed nanoparticles. Despite the clustering of the nanoparticles, the higher zero-shear viscosity observed at low loadings (2 and 4 wt% $SiO_2$) and neutron scattering data suggest that the PE-g-$SiO_2$ additives formed a percolated network, thus improving melt stability. This effect was not seen at 6 wt% loading, which was attributed to agglomeration of the nanoparticles. The maximum enhancement in modulus (55% increase) was observed at 20 wt% silica loading in the nanocomposite. The optimal impact strength was observed at 13 wt% loading of silica. Current efforts have been focused on developing grafting techniques that improve the uniformity of grafts on the nanoparticle surface, and allow for characterization based on grafting density.

## Future Plans

On the computational front, simulations of crystallization in the presence of families of additives such as those isomorphous with the diamond cubic lattice (including binary compositions like ZnS, GaN) and the hexagonal graphene lattice will continue. Heuristics for optimal additive performance will be extracted from the dataset of simulation results. A conclusive model for nucleation and crystallization induced by additive materials will be developed which takes into consideration additive design parameters such as crystal structure and atomic interaction strength. On the experimental front, dispersion of graphene nanoplatelets in HDPE and assessment of impact on structural, melt and solid state properties will be performed, and the results related back to computational results. .

## Broader impact

The project is training one graduate student (Alex Bourque). The results of computational studies for the polyethylene/C50 system were reported at the ACS National Meeting (San Francisco, CA, Aug.10, 2014). A second presentation is scheduled for the March 2015 meeting of the APS (San Antonio, TX). In addition, Alex will gain experience as a summer intern at ExxonMobil Research and Engineering in summer, 2015.

## Data Management and Open Access

All computational results are stored locally at MIT in accordance with the Data Management Plan. Results on studies of polyethylene/C50 are currently being prepared for publication. Raw computational data will be stored and made publicly available via DSpace, MIT’s data archiving service, at the end of the project.

## References

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## Publications

(None)

# High-Throughput Simulations and Experiments to Develop Metallic Glasses

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**Keywords:** metallic glasses, combinatorial sputtering, high-throughput ab-initio simulations,

## Project Scope

We combine high-throughput computing, combinatorial materials synthesis and characterization to develop bulk metallic glasses (BMGs) – a class of materials that can be regarded as high-strength metals that can be processed like plastics. Rather than trying to directly simulate glass formation, we integrate experiments and computations to understand which structural and energetic aspects of the liquid and crystalline state correlate best with glass-forming ability and properties of the glass, and use these correlations to search for new glass-forming compositions. Specifically, we seek correlations between glass-forming ability and the competing crystalline phases, which can be calculated in a high-throughput fashion from first principles. Here we identify the number of competing crystalline phases, their structural characteristics, and their energetics.

## Relevance to MGI

We use a closed-loop approach (see Figure) of combinatorial ab initio simulations, combinatorial synthesis of sputtered composition spreads, and high-throughput characterization methods. Within such an approach a vast number of experimental and computational data will be generated which we will datamine to identify correlations between the competing crystalline phases and the ability of the alloy to form a glass. Identifying correlations is a key aspect of our research and we use these correlations to search, through combined computational and experimental means for new glass forming compositions.

## Technical Progress

We currently focus on Zr-Cu, a well-studied binary BMG forming system. Our ab initio simulations have indicated large differences in density of states of competing crystalline phases as a function of composition. These density of states are calculated by considering up to 1000 different configurations and determining their distribution on the energy scale. These calculations are carried out in the relevant composition range and organized by energy and structural similarity for all considered compositions in one system. In order to determine correlations we sputter a broad compositional range and we are using combinatorial nano-calorimetry to quantify the glass forming ability of the various compositions. Specifically, we determine the glass transition temperature, crystallization temperature, and solidus and liquidus temperatures as a function of composition for approximately 30 different alloys in one experiment. This high-throughput approach enables us to identify correlations and trends in the composition dependence of thermophysical properties. For some selective alloys, we have made bulk samples to determine the competing crystalline phases which can be stable or metastable. Our preliminary conclusion is that best glass forming compositions are present at compositions where the number of crystalline phases that compete with glass formation has a maximum.

## Future Plans

We will continue mining our data to confirm a correlation between the number of competing crystalline phases and glass formation. This will be done in a variety of systems including metal-metal, and metal-metalloid based BMG formers. Specifically, in order to understand the typically significant improvement of glass formation when expanding from binary to ternary or higher ordered systems, we will be expanding our search to multicomponent systems. Here we will consider aluminum-based metallic glasses, a technological highly desirable yet challenging system. An experimental strategy that we have been pursuing beyond the number of crystalline phases is to identify characteristics in the microstructure that indicates good glass forming ability. Experimental data of the structure and thermophysical properties will be data mined to close the feedback loop and improve the predictability of our approach.

### Broader impact

Our developed methodology will accelerate the pace of discovery and deployment of metallic glasses, which most aspects can be expanded to other material classes. The potential development of technologically relevant BMGs, particularly those that are based on Cu or Al can be expected to have a lasting impact on society similar in magnitude to thermoplastic polymers in the previous century. The students involved in this project are exposed to an advanced and more integrated approach of materials development.

### Data Management and Open Access

To provide a generally enhanced knowledge base to the scientific community and make it possible to tackle the grand challenge in materials development more effectively, we will openly share data among the community through the AFLOWLIB.org consortium, thereby will contribute to the impact of the project.

# Acoustically Transformative Materials

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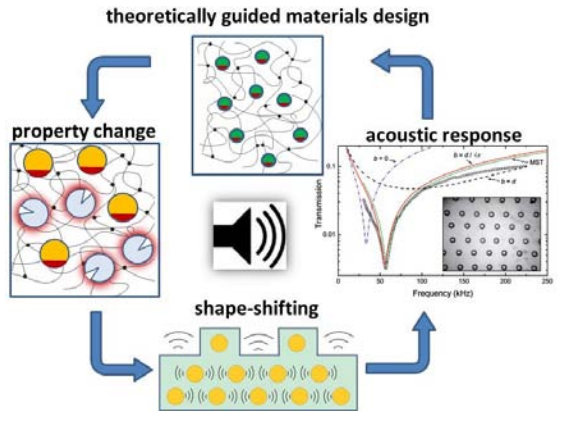
**Keywords:** Polymers, Elastomers, Molecular Design, Stimuli-responsive, Acoustics, Shapeshifting

## Project Scope

The goal is to create novel class of materials that can be activated, actuated, and navigated remotely using acoustic fields in a programmable and time-resolved manner. Theoretical predictions will guide synthesis of novel polymer architectures possessing superior elasticity and distinct acoustic response. Particularly challenging is the feedback between the material-dependent acoustic characteristics and acoustically-triggered changes of materials properties. By understanding these correlations, we will develop stimuli-responsive materials that would not only respond to sound by changing their physical properties (density, shear modulus, and shape), but also actively manage acoustic performances, such as tunable phononic band gaps and sound attenuation.



Understanding the feedback between the material-dependent acoustic characteristics and acoustically-triggered changes of materials properties.

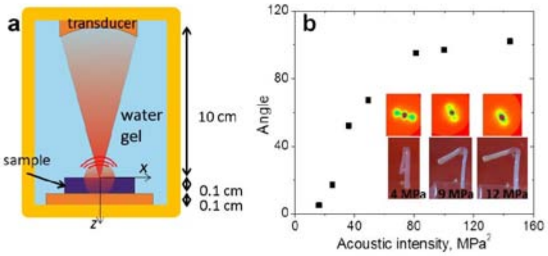
## Relevance to MGI

The proposal has two strategic goals: First, develop fundamental understanding of multi-scale correlations between complex macromolecular architectures (rings, brushes, and networks) and mechanical properties of materials assembled of these molecular mesoblocks. The goal is to provide theoretical guidelines for the synthetic design of materials with extraordinary broad range of elasticity, strength, and toughness that are not available in conventional polymer systems. Second, study interaction of sound waves with the designer materials and explore different activation mechanisms that shift density, modulus, and shape. These studies will provide feedback to theory and validate adjustments in molecular design.

## Technical Progress

A theory of viscoelasticity of cylindrical brushes and non-catenated rings has been developed. For bottlebrush elastomers, we predict that the shear modulus of reduces as $G \sim (\phi_g N_{sc}\, N_{bb})^{-1}$, where $\phi_g$ is the grafting density, $N_{sc}$ and $N_{bb}$ are the degrees of polymerization of the side chains and backbone, respectively. This reduction is enabled by an exceptionally low density of chain entanglements. To verify these predictions we have synthesized a series of cylindrical brushes with an extraordinary long backbone ($N_{bb} \cong 2000$), controlled $\phi_g$, and systematically varied $N_{sc}$. We have corroborated the entanglement plateau modulus of bottlebrush melts decreases with $N_{sc}$ as $G_e \sim N_{sc}^{-3/2}$ which allows pushing the modulus of solvent-free elastomers down to 100 Pa. For polymer rings, we predict that the storage modulus varies as $\sim M^{-1}$, where $M$ is the number of monomers between crosslinks. Upon extension, the ring elastomers exhibit non-linear stress-strain behavior due to sequential unfolding of hierarchic loops. These adaptive polymer matrixes will enable actuation of acoustically responsive fillers that carry multiple functions when exposed to ultrasound: They will expand, dissociate, and assemble to generate, enhance, and modulate acoustic signal.

We have synthesized stimuli-responsive microcapsules enabling controlled expansion under ultrasound heating, which results in drastic changes in modulus and density of a composite material. By controlling the chemical composition of the microcapsule core, we can control both the onset temperature of expansion within a range of 80-150 °C and the expansion ratio within a range $V/V_0=1\text{-}30$.Pulse high-intensity focused ultrasound (HIFU) have been applied to initiate shape transformations in two systems: semi-crystalline elastomers and microbubble-filled composites. As a successful proof-of-concept HIFU was applied to actuate unfolding of a hairpin of a semi-crystalline elastomer monitored by SAXS. We have quantified the effect of acoustic pressure, pulse length, and frequency on sample temperature and shape alteration as a function of time.



**Acoustic actuation.** (a) A sample of a shapeshifting polymer is imbedded into an aqueous matrix (gel). (b) A polymer hairpin unfolds with increasing intensity of an acoustic pulse.

## Future Plans

The overall strategy is comprised of three interrelated tasks. **Task 1** is to design solvent-free responsive polymer matrix, which demonstrates a balanced combination of (i) low modulus ($<10^5$ Pa) matching biological tissues, (ii) high extensibility to accommodate cavitation, (iii) high elasticity to enable efficient transmission of local transformations to a macroscopic scale. **Task 2** is to design acoustically active fillers and study interaction of sound with the designer composites. Examples of the acoustic triggers include (i) melting of crystallites which significantly decreases the shear modulus and enables a shape shift, (ii) expansion of 0.1−10 μm microcapsules resulting in drastic changes in compressibility and density, and (iii) dissociation of hydrogels resulting in softening of the matrix and solvent release. **Task 3** is to demonstrate that an acoustic field can switch materials properties and, vice versa, that a responsive material can modulate propagation of sound through a soft matter. We will explore potential for practical applications of acoustically actuated objects. (i) We will design composites that will switch shape and volume in a programmable fashion both in space and in time. These acoustically-triggered shapeshifting may be vital for promoting self-healing of cracks and permeation of particles through obstructions. (ii) We will explore intriguing opportunities for sono-lithography and non-invasive surgery, where object's shape can be altered locally in a sequential order. (iii) We will design tunable phononic band-gap materials, and study modulation of the acoustic properties by controlling spatial arrangement, individual dimensions, and mechanical properties of expandable microcapsules.

## Broader impact

This project provides with an extraordinary opportunity to develop a *new direction in materials design* wherein fundamental changes in materials properties are activated by sound waves that concurrently shift acoustic, optical, and geometric characteristics of macroscopic objects. The interdisciplinary nature of the project will ensure maximum opportunity for (i) integrating science and education through interdisciplinary training of junior researchers, (ii) enhancing diversity by broadening participation of underrepresented groups, and (iii) fostering infrastructure for collaborative research.

## Data Management and Open Access

All primary data will be made publically available by the time of publication or the end of the funding period via journal articles, reports to NSF, and data archives at UNC and CMU. Other research products, such as instrumentation, data sets, and software will be either shared upon request or made publically available. In the latter case, the PI will consult with NSF concerning the right to use the data prior to opening it up to wider use. If permitted, we will develop a public database in which raw data may be deposited. Sharing unpublished data with our peers is vital for future collaborations.

# Nanoporous Materials Genome: Methods and Software to Optimize Gas Storage, Separation, and Catalysis

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**Keywords:** Porous Materials • High-throughput screening • Electronic structure methods • Molecular simulation • Validation experiments

### Project Scope

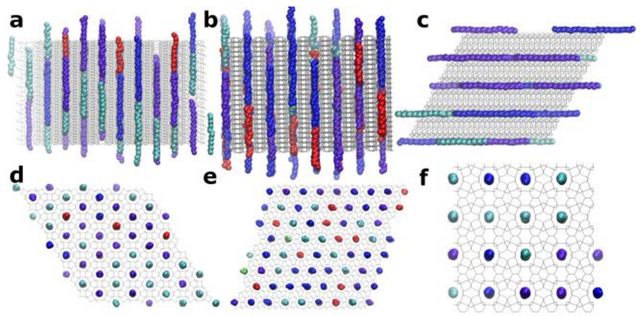
The Nanoporous Materials Genome Center (NMGC) discovers and explores microporous and mesoporous materials, including **metal-organic frameworks** (MOFs), **zeolites**, and **porous polymer networks** (PPNs). These materials find use as storage and separation media and catalysts in many energy-relevant processes and their next-generation computational design offers a high-payoff opportunity. Towards that end, the NMGC develops state-of-the-art predictive modeling tools, databases, and web-based repositories, and employs them to increase the pace of materials discovery.

### Relevance to MGI

The goals of the NMGC are advanced by a tight collaboration between leading experimental groups in the synthesis and characterization of nanoporous materials and of computational groups with experience in molecular simulation, electronic structure calculations, and theory. The majority of the completed projects resulted from iterative feedback where computational modeling was instrumental for understanding the function of specific nanoporous materials or for discovering materials with optimal properties for subsequent synthesis.

### Technical Progress

The NMGC research efforts have already led to more than 40 publications. In this presentation, we highlight the key achievements of five application projects and one web tool that are central to the goals of the NMGC. (a) Experimentally refined crystal structures for MOFs often include solvent molecules and partially occupied or disordered atoms. This creates a major impediment to applying high-throughput computational screening to MOFs. To address this problem, we construct a database of MOF structures that are derived from experimental data but are immediately suitable for molecular simulations.[6] The computation-ready, experimental (CoRE) MOF database contains ~5000 porous structures with important physical and chemical properties including the surface area and pore dimensions. To demonstrate the utility of the database, we compute the adsorption of methane and of the five hexane isomers on all CoRE MOF structures, and investigate the structural properties governing methane storage capacity and selectivities for specific hexane isomers. (b) MOFs are actively being explored as potential adsorbed natural gas storage materials for small vehicles. Experimental exploration of potential materials is limited by the throughput of synthetic chemistry. To complement and guide these experimental efforts, we develop a computational methodology using known chemical transformations *in silico* to identify MOFs with high methane deliverable capacity. We efficiently search the composition and conformation space of organic linkers for nine MOF networks, finding 48 materials with higher predicted deliverable capacity (at 65 bar storage, 5.8 bar depletion, and 298 K) than MOF-5.[2] (c) Screening sorbents and catalysts for complex mixtures composed of large, articulated molecules, where advanced algorithms are required for sampling the distribution of thousands of conformers, or polar, hydrogen-bonding molecules, where an accurate description of electrostatics and the resulting mixture non-idealities are of paramount importance, has so far been an intractable problem. Enabled by a multistep screening workflow, efficient sampling algorithms, accurate force fields, and a two-level parallel execution hierarchy utilizing up to 131,072 compute cores on Mira, a leadership-class supercomputer at Argonne National Laboratory, we perform high-throughput screening for two energy-related applications and identify zeolites with exceptional selectivities for ethanol purification from aqueous solution and the transformation of alkanes with 18-30 carbon atoms.[3] (d) Enzymatic heme and non-heme high-valent iron-oxos are known to activate very strong C–H bonds with relative ease, yet duplicating this impressive reactivity in a synthetic system has been a formidable challenge. We demonstrate that a MOF featuring site-isolated iron centers in a weak-field ligand environment can convert ethane into ethanol and acetaldehyde using nitrous oxide as the terminal oxidant. Using electronic structure calculations we show that the active oxidant is a high-spin, $S = 2$ single-state iron(IV)-oxo acting via a $\sigma$ -pathway and elucidate all steps in the mechanism.[18] (e) Quantum mechanical computations can provide useful guidance in prioritizing the synthesis of optimal materials for a given gas separation; we use such computations to identify a new MOF with open vanadium sites that is of potential utility for the separation of dinitrogen from other light gases, such as methane or dioxygen. The differential adsorption energy $\Delta E = E_{\mathrm{ads}}(N_2) - E_{\mathrm{ads}}(CH_4)$ is larger for V-MOF-74 compared to analogous M-MOF-74 materials with other metals. Orbital analysis reveals that two types of interactions, the $\sigma$ donation and $\pi^*$ backbonding, are responsible for the strong V-$N_2$ bond.[31]



Snapshots of alkanes inside ATO (a,d), MTW (b,e), and PCOD-8113534 (c,f) with adsorption occurring from a liquid phase containing an equimolar mixture (linear C18, C24, C30, and branched C18 isomers in cyan, purple, blue, and red, respectively) at $T = 573$ K and $P = 3$ MPa.

## Future Plans

The NMGC team will continue its collaborative endeavors to discover nanoporous materials with optimal gas storage, separation, and catalytic abilities and to use an integrated computational/experimental approach for unraveling structure/chemistry/function relationships. Two provisional patent applications resulting from NMGC discoveries have been filed, and the NMGC will further develop these and other nanoporous materials. The collaborative NMGC activities have also strengthened the training of a large number of postdoctoral associates and of graduate, undergraduate, and high school students.

## Data Management and Open Access

In collaboration with the Materials Project, the NMGC has developed the *Nanoporous Materials Explorer*. This openly accessible web-based tool aids materials discovery and also serves as repository for computational and experimental data generated by the NMGC. The CoRE MOF database is also available for download.

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# Simulation-Driven Design of Highly Efficient MOF/Nanoparticle Hybrid Catalyst Materials

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**Keywords:** Catalysis, regioselectivity, oxidation, hydrogenation, metal-organic framework

## Project Scope

This project seeks to exploit recent advances in synthesizing nanoporous materials via a true building-block approach to conceive, synthesize, characterize, and test new heterogeneous catalysts that exhibit enzyme-like control in demanding chemical transformations. Catalytically active metal nanoparticles are encapsulated within metal-organic framework (MOF) crystals. MOFs are nanoporous materials synthesized in a building-block approach from metal nodes and organic linkers. Enshrouding metal nanoparticles within MOFs prevents their agglomeration and allows control over reactant access to their surfaces. In this project, molecular-level modeling is used to guide the selection and synthesis of appropriate metal surfaces and MOF channels for two important classes of reactions. The objectives of this project are 1) to develop new ways of synthesizing heterogeneous catalyst materials with structural control ranging from the atomic level to the particle level and 2) to demonstrate how new levels of synthetic control, combined with predictive molecular-level modeling, can drastically decrease the development time of new catalytic materials.

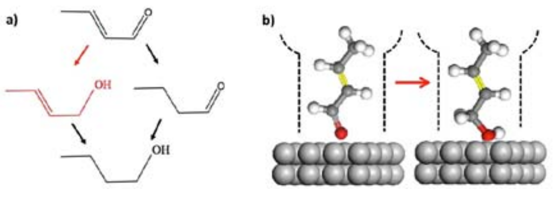

**Figure.** a) Hydrogenation of crotonaldehyde (top) to crotyl alcohol (red), an unsaturated alcohol, is the desired reaction. Normally, however, hydrogenation leads to the saturated alcohol or aldehyde (black). b) In a sterically constrained reaction path, the $\alpha$-$\beta$ unsaturated bond (yellow) is inaccessible, thus only the desired unsaturated alcohol is produced.

## Relevance to MGI

The building-block approach to MOF synthesis and the accompanying possibility for the synthesis of an almost unlimited number of materials clearly create exciting possibilities for catalysis, as well as other applications such as chemical separations, gas storage, sensing, and drug delivery. But it also creates the following challenge: how does one identify the most promising structures, among the millions of possibilities, for a particular application? In this project, we are developing computational tools to generate millions of MOFs on the computer and computationally predict their properties to find the right materials with the right properties for hybrid MOF/nanoparticle catalysts. This computational approach will greatly accelerate the rate at which we can discover and develop new materials for catalysis, as well as other applications of nanoporous materials.

## Technical Progress

We successfully encapsulated Pt nanoparticles of 150 nm within ZIF-8 particles and used them to demonstrate regioselective hydrogenation of (only) the terminal double bonds of 1,3-dienes. For example, hydrogenation of 1,3-hexadiene yielded only 3-hexene. We have also performed DRIFTS studies of CO and Pt@ZIF-8 and found that end on (Pt-CO) and bridging (Pt-CO-Pt) peaks are red shifted approximately 50 $cm^{-1}$.

This indicates electronic donation into the Pt nanoparticle. We surmise that the ZIF imidazolate ligands are coordinated to the Pt nanoparticle and the increased electron density is being back bonded to the CO antibonding orbital. Increases in electron density in Pt nanoparticles has been demonstrated to increase reactivity toward C-O bond cleavage reactions.

Encapsulation of sub-1.5 nm Au nanoparticles within ZIF-8 results in a composite for regioselective hydrogenation of crotonaldehyde to crotyl alcohol. See the figure. Size-selective hydrogenations of 1-hexene and cis-cyclooctene and microscopy (SEM and line-scan EXD) suggest that the Au nanoparticles are well encapsulated with in the ZIF composite. Although overall conversion of crotonaldehyde to crotyl alcohol was low (ca. 15%), selectivity for the unsaturated alcohol was extremely high.

We have proposed and developed a "featureless" ring model based on chemically inert helium atoms to computationally investigate reactions under the steric constraints imposed by the MOF pores in our MOF/nanoparticle materials. We have tested that the ring model only introduces steric effects and not spurious chemical effects. Specifically, we compared adsorption and reaction energies calculated using density functional theory (DFT) on a palladium surface model with and without the ring. As anticipated from the small interaction energies between the ring and the surface (~0.1eV/He atom), adsorption and reaction energies involving only small species such as "O" and "H" are unaffected by the presence of the ring. For instance, O and H adsorb at fcc sites with adsorption energies of -1.4 eV and -0.5 eV, respectively, and they combine to form OH (i.e. $O^* + H^* \rightarrow OH^*$) with a reaction energy of -0.14 eV. On the other hand, species large enough to be sterically affected show different adsorption and reaction energetics in the presence of the ring. Notably, the primary CH activation changes from exothermic under unconstrained conditions ($C_4H_{10}^* \rightarrow C_4H_9^* + H^* + 0.31$ eV) to endothermic under sterically constrained conditions ($C_4H_{10}^* + 0.04$ eV $\rightarrow C_4H_9^* + H^*$).

We developed a topologically-based ("top-down") automated computational approach to generate MOF structures that could potentially serve as enshrouding materials for our catalysts nanoparticles. This approach complements a previous "bottom-up" approach developed in our group, and it now allows more control on the generated structures. Using the new tool, we generated a database of ~13,500 unfunctionalized MOFs spanning ~40 distinct topologies. We aimed to include topologies that could make use of building blocks known to (typically) result in highly stable structures in order to increase the probability for their applicability under the relatively harsh catalytic conditions. Importantly, we demonstrated the capability of the generator to produce zeolitic imidazolate frameworks (ZIFs), which are a subclass of MOFs renowned for their stability.

## Future Plans

In order to study the effect of pore aperture size on the catalysts selectivity, we are encapsulating Pt nanoparticles into different MOFs with a range of pore apertures. Extensive characterization of the catalyst materials is also underway, as well as additional catalytic testing. We are investigating both hydrogenation and oxidation reactions under steric constraints using DFT for Pd and Ag surfaces.

## Broader impact

This project supports the training of 2 graduate students, 2 post-docs, and 1 undergraduate student. The team is highly interdisciplinary and includes both experimentalists and modelers. The entire team meets monthly (including the members from Clemson via Skype), in addition to more frequent meetings of the students and post-docs with their faculty mentors. The students and post-docs are forming a closely knit team and being trained in a highly interdisciplinary research environment.

## Data Management and Open Access

The database of MOFs will be made publicly available. We already make our molecular simulation codes publicly accessible.

# Theory-Enabled Development of 2D Metal Dichalcogenides as Active Elements of on-chip Silicon-Integrated Optical Communication

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**Keywords:** Transition metal dichalcogenides, phase transitions & control, growth, optoelectronic devices

## Project Scope

This project explores the properties and manufacturability of 2D metal dichalcogenide single-layer films utilizing as a testbed an optical waveguide structure that at the same time allows facile evaluation of materials properties and offers straightforward extension towards the first deep subwavelength, plasmonic enhanced, TMD laser potentially electrically driven. Computationally, this project investigates systematically the stability of structural phases and method to induce phase transitions in the materials system addressed. During the first month of this project, we have synthesized single layer films of $MoS_2$, $MoSe_2$, $MoTe_2$, $WSe_2$, and $WS_2$ as well as several of their alloys. This sets the stage for transport measurements and characterization of their optoelectronic properties.

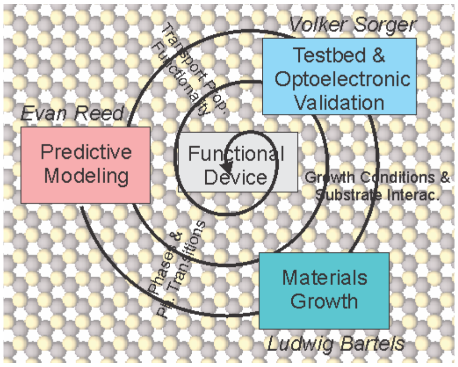


**Figure 1.** Schematic Overview of this Project

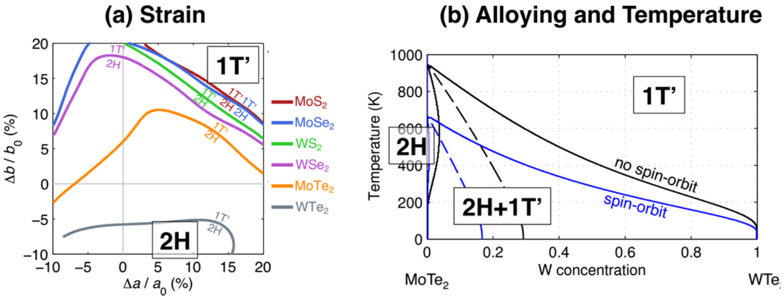


**Figure 2.** Stability of the 1T' vs. 2H phase of different transition metal dichalcogenides as a function of strain (a) and compositions (b).

## Relevance to MGI

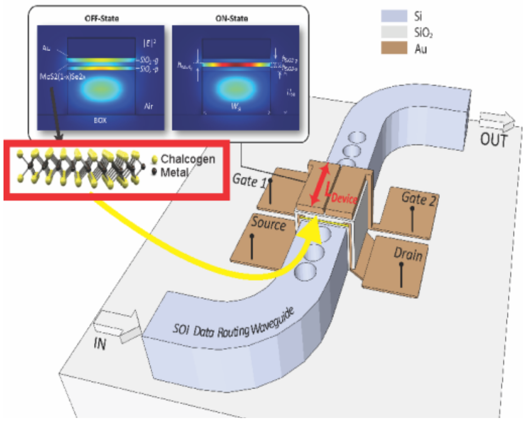
Knowledge about fundamental properties (bandgap, etc.) of metal dichalcogenide materials, even at the single-layer limit, is readily available, yet in order to serve as the foundation for the design of manufacturable optoelectronic devices, a much broader range of properties need to be available by validated computational means (Fig. 2). These include growth conditions, phase diagrams and surface interactions. For instance, $MoTe_2$ is a transition metal dichalcogenide material that has attracted much attention as 2D semiconductor, yet we find that under typical growth conditions it attains a metallic phase T' at the single layer limit and not the semiconducting 2H phase known at room temperatures. This provides both a challenge and an opportunity: *in-situ* growth of single-layer films of $MoTe_2$ into functional devices needs to include a guided transition towards the semiconducting room-temperature phase as a processing step, yet lateral semiconductor/metal transitions can be part of a compositionally-homogeneous single layer film, if ways are found to stabilize locally one phase over the other. This project aims at predictively revealing such phenomena to serve as a basis for manufacturing and application choices of materials that obtain their importance as 2D layers. To do so, this ties together computational work that highlights the mentioned aspects of metal dichalcogenide films, growth efforts that realize these films and the development of a facile testbed that offers *in-situ* growth and high-throughput application-near validation. Our work in this area will be leveraged by many other researchers to accelerate design of 2D materials for the broader spectrum of potential applications.

## Technical Progress

During the first half-year of this project we have made substantial advances in all three areas of this project. Computational we have mapped out a significant portion of the compositional space with regards to stability, and phase transition, which provides us with a set of practical avenues to exert phase control (Fig. 2). The growth effort follows closely along realizing all of the well-established transition metal dichalcogenides and some of their alloys on a variety of substrates. With regards to validation, with have started the fabrication of the most-fundamental waveguide-best testbeds and have conducted preliminary growth studies on them. Extensions of them towards plasmonically-enhanced laser cavities are currently in the modeling stage. Additionally, a 3D structure motivated by mechanical flexibility of 2D materials was proposed for high efficiency photovoltaic cells.[1]

## Future Plans

For this new project, the proposed work includes investigations (a) to map-out the chemical and thermodynamic space of 2D materials to enable engineering of the growth parameters and materials properties, (b) to synthesize 2D materials and their alloys *in-situ* within optoelectronic testbed environments, and (c) to validate computational transport and device properties thereby achieving accelerated prototyping. Manufacturability is one of the most pressing concerns in 2D materials and we address this challenge head-on by exclusively utilizing films that are grown inside lithographically prepared testbeds; computational work will directly address phase transitions, substrate interactions and other aspects affecting fabrication. While single-layer films cannot readily exceed absorption of ~3%, we combine them with structures that can increase this value significantly such as nanoscale plasmonically enhancing cavities.



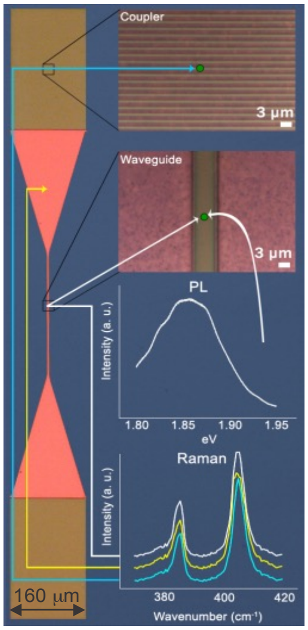


**Figure 3.** Testbed approach for rapid functional 2D material characterization. (left) plasmonic waveguide integrated light source, (right) preliminary data of waveguide-integrated PL from $MoS_2$.

## Broader impact

Broadly band-gap tunable, *in-situ* on silicon growable, atomically thin light sources and sensors can have a transformative impact on on-chip and inter-chip optical interconnects that directly stem from the intrinsic properties of the materials involved. Incorporation of an accredited Hispanic Serving Institution (UCR) provides impact through human resource development and integration of minority individuals (7 of Bartels' graduate students are either Hispanic or African American). Through this project, they will have access to and interaction with premier research institutions, such as through recent visits to Stanford. Outreach to Congress in person, and to the general public through reviews in outlets like Financial Times and Scientific American by PI and co-PIs, respectively, strengthen public appreciation of research. In combination with interdisciplinary interaction, development of two untenured faculty and a proven pathway to outreach, this project is well aligned with NSF's broader impact goals.

## Data Management and Open Access

Data is being shared with the public in classical ways. In addition, we plan to establish an online database for 2D materials to facilitate the acceleration of 2D materials developments by other researchers.

## Publications

1. M. Taher-Sima, and V. J. Sorger, *2-D Material-based Spiral Solar Cell*, IOP Nanotechnology (submitted).

# EFRC Center for Bio-Inspired Energy Science

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**Keywords**: bio-inspired materials, colloidal machines, charge transport, artificial muscle, artificial organelles

## Project Scope

The goal of the Center for Bio-inspired Energy Science (CBES) is to develop artificial materials and systems that take inspiration from biology to optimize the way we use energy and interconvert between different energy forms, for example converting chemical energy into mechanical energy the way muscles do in living organisms. Our team members have innovated in the areas of self-assembly, the interface of biology and materials science, as well as in theory and simulation of materials. CBES is scientifically organized into three main thrusts on materials with biomimetic functions, colloidal machines, and biomimetic modes of charge transport.

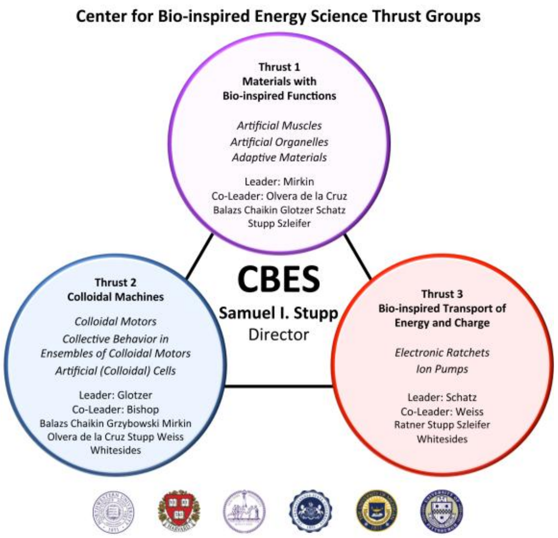

**Figure.** Scientific organization of the Center for Bio-inspired Energy Science.

## Future Plans

**Thrust 1** will focus on materials with biomimetic functions related to inter-conversion between chemical and mechanical energy (as muscles do), particles inspired by biological organelles that utilize feedback mechanisms to mediate chemical reactions, and adaptive materials. **Thrust 2** investigates active matter in the form of colloidal machines, which are systems of nanometer to micrometer scale colloids that behave collectively far from equilibrium. **Thrust 3** explores artificial matter that could exhibit bio-inspired mechanisms of electron and ion transport, such as those of transmembrane ion pumps, ratchets, and photosynthetic systems.

## Relevance to MGI

Half of the investigators at CBES are theoreticians and the other half are experimentalists. The common thread of its research portfolio is the development of carefully designed materials and devices inspired by biological systems using highly integrated experimental and theoretical strategies.

# Computationally Driven Targeting of Advanced Thermoelectric Materials

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**Keywords:** Thermoelectrics, electronic structure, charge carrier transport, thermal transport

### Project Scope

This project seeks to accelerate the discovery of new thermoelectric (TE) materials by combining theory, experiment and high-throughput computations. To this end, we are (i) developing a computational infrastructure for TE material search, (ii) validating this approach through experimental measurements and (iii) applying this approach in a high-throughput format to a broad range of known, crystalline materials. The resulting database of experimental, computational and structural results will be analyzed to reveal material design strategies and will be open to the community through a dedicated TE materials design website.

### Relevance to MGI

Development of TE search and design strategies requires an iterative feedback loop between synthesis and characterization on one end, and theory and computations on the other. This is due to the non-trivial nature of electron and phonon transport and challenges facing the standard electronic structure calculations. To overcome this challenge, experimental results are integrated into a semi-empirical model that is built off of ground state electronic structure calculations. In the first year of this project, we have demonstrated a closed cycle between theoretical predictions and experimental validation of these predictions.

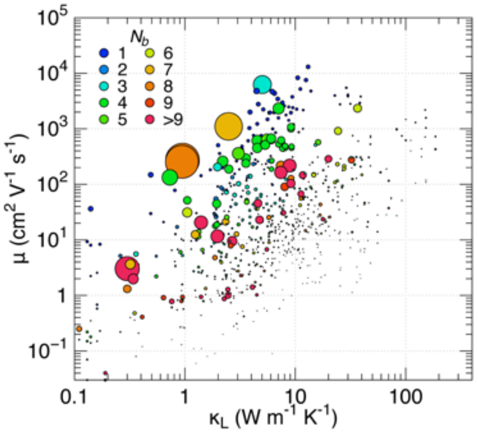

**Figure 1.** The development of semi-empirical models for lattice thermal conductivity ($\kappa_L$) and mobility ($\mu$), along with band degeneracy ($N_b$) enables high-throughput assessment of materials for thermoelectric performance (circle size).

### Technical Progress

To date, our focus has been on building the foundational infrastructure for high throughput TE material assessment. The primary challenge is addressing scattering phenomena in a computationally efficient manner. To address the challenges associated with direct computations of charge carrier mobility ($\mu_o$) and lattice thermal conductivity ($\kappa_L$), we combined classic scattering theory, a large body of experimental data and electronic structure calculations; together these enabled the development of semi-empirical models that include only the quantities that are readily available from the standard density functional theory calculations. Consideration of the Boltzmann transport equations within the relaxation time approximation allows one to separate the intrinsic materials properties contributing to the TE figure of merit (zT), which are described by the quantity $\beta \sim \mu_o\, m_{DOS}^{3/2}/\, \kappa_L$, with $m_{DOS}$ being the charge carrier DOS effective mass. We recently presented these semi-empirical models and our first high-throughput results in *Energy & Environmental Science* (Figure 1).[1] These results demonstrated the efficacy of $\beta_{SE}$ in correctly identifying known TE materials and in high-throughput screening for new candidate materials. Ultimately, our approach offers a direct connection between ab-initio calculations and experimentally measured quantities by deriving semi-empirical relations for $\mu_o$ and $\kappa_L$, which are nearly inaccessible to high-throughput computations. Experimental work is feeding back to improve the accuracy of these initial predictions; we are targeting compounds with a range of predicted properties (e.g., extremely low and high $\kappa_L$) through solid state synthetic routes and TE property measurements. Compounds with potentially promising TE performance are being pursued. The results of these calculations and associated model development have been made available to the public through an on-line material design 'laboratory'. The Thermoelectrics Design Lab (TEDesignLab) is envisioned as a full design environment for TE materials offering both the raw data, combined experimental and computational results, and empowering the users with the broad spectrum of tools for analysis and data mining. In addition, TEDesignLab will also make all computer codes developed from the project available to the public.

### Future Plans

With the foundation developed in the first year, we will continuously grow the set of materials under consideration, and assess their potential for TE performance against our $\beta_{SE}$ metric. We will continue to pursue experimental verification of the semi-empirical models employed in $\beta_{SE}$. As the search progresses, we will continue to add additional material descriptors that are relevant for TE performance (e.g., dopability, stability). To further deepen our understanding of the transport physics that drives $\beta_{SE}$, we will directly calculate charge carrier (electron-phonon) and phonon relaxation time in candidate materials. Finally, $\beta_{SE}$ will be expanded to non-band conductors (e.g., transition metal oxides) to capture their potential for TE performance. As this project continues, our TEDesignLab website will continue to serve as the main front-end of our project allowing the general public the access to all the growing data, the continuously updating $\beta_{SE}$ metric. At this point, the TEDesignLab is primarily a database repository and visualization platform. In the future, we will grow this website to include data mining functionalities. Such advanced functionalities seek to turn the website from simply a 'warehouse' of information into a true *laboratory* that allows the public and scientific community to explore material property trends in the context of TE materials.

### Broader impact

The team is engaged in a suite of broader educational objectives to foster the MGI spirit. We have been invited to present this work at material science and material informatics conferences. The semi-empirical approach we have developed to overcome high throughput issues with scattering of electrons and phonons is expected to be valuable throughout thermal and electronic materials. The integration of material science and data mining is being integrated into courses within Physics, Material Science and Computer Science at CSM, Northwestern and CU Boulder, respectively. On a personal level, we are learning to communicate effectively between disciplines that do not often overlap. To foster an appreciation at the undergraduate level of the interconnectedness between these disciplines, we have had several undergraduate (including community college) students work on topics within this project.

### Data Management and Open Access

One important goal of this project is to make all the computational and experimental data, corresponding data analysis functionalities, and computer codes publicly accessible. To this end, we have developed www.tedesignlab.org. Through this website, users can import and export both computational and experimental data about specific or a subset of TE materials, search for materials with certain properties, and visualize materials properties. We are in the process of integrating various data analysis functionalities into the web interface as well as the codes developed to compute, analyze and/or mine the data. These functionalities are customized to work smoothly with the computational and experimental data hosted at our website. Instead of downloading all the data and writing their own analysis codes offline, users will be able to launch dedicated data analysis tasks on the fly, and analysis results can be stored and easily compared. In summary, with a suite of functionalities including data import/export, search, visualization, and analysis capabilities, we intend to make www.tedesignlab.org the primary public repository and design lab for advanced TE materials research.

## Publications

1. J. Yan, P. Gorai, B. Ortiz, S. Miller, S. Barnett, T. O. Mason, V. Stevanovic, and E. S. Toberer, *Material descriptors for predicting thermoelectric performance*, Energy & Env. Sci. *accepted*.
DOI: 10.1039/C4EE03157A

# Center for Next Generation of Materials by Design (CNGMD) Energy Frontier Research Center

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**Keywords:** metastability, polymorphs, alloys, energy materials, in-situ characterization

**Project Scope**

The overall mission of the CNGMD is to dramatically transform the discovery of functional energy materials through multiple-property search, incorporation of metastable materials into predictive design, and the development of theory-guided materials synthesis. We couple first-principles theory with state-of-the-art synthesis and *in-situ* characterization to understand and predict structure, properties, and phenomena at the molecular, nano-, and meso-scales. We are focused on the discovery and synthesis of novel functional semiconductor materials including non-equilibrium structures for solar energy conversion, solid-state lighting, energy storage, and related technologies—all areas that are in need of transformative materials.

**Relevance to MGI**

This EFRC is specifically designed to eliminate several critical scientific gaps that must be overcome before computational materials and process design becomes a robust tool set delivering new functional materials and synthesis approaches for energy based applications specifically addressing: 1) ***multiple-property design***, 2) ***accuracy and relevance***, 3) ***metastability***, and 4) ***synthesizability***. Combining these elements will create an approach that will expand and accelerate the discovery of experimentally accessible functional materials for a broad range of energy applications. These methodologies will also impact the broader area of materials discovery including other areas of energy conversion, storage or utilization.

**Technical Progress**

This EFRC started in September 2014 as a newly awarded project. Initial studies will concentrate on new materials for photo-active absorbers, transparent conductors, contacts and electrodes.

**Future Plans**

The goals of the CNGMD EFRC are to:

1) Design and discover new energy-relevant materials with targeted functionalities by integrating theory, high-throughput computation, synthesis, and characterization
2) Develop foundational theoretical, synthesis, and characterization tools to enable the next generation of Materials by Design
3) Incorporate functional metastable materials into Materials by Design and establish ranges for materials metastability as a function of the chemistry and structure arising from defects, polymorphs, and solid solutions (alloys)
4) Develop a systematic theory-driven approach to guide the synthesis of new materials—including metastable systems—by coupling theory and state-of-the-art *in-situ* characterization to probe materials growth pathways
5) Promote and disseminate the Next Generation of Materials by Design to the broader materials science community.

Our efforts on multiple property search centers around inorganic solar materials. Our work on foundational tool development is aimed at rapidly and accurately calculating and measuring key opto-electronic properties such as band-gap energies and the surface energy as a function of crystal face orientation which can be a key step in computational interface design. Predictive theory typically targets the materials at thermodynamic equilibrium, i.e. at the bottom of the convex hull (Figure 1). Many functional materials, however, including those for solar energy conversion, energy storage and light emission are in fact metastable. We will investigate three primary classes of metastable materials, all of which have significant potential for new functionality:

1. Polymorphs – materials that are structurally different but compositionally identical
2. Alloy systems that can be crystalline or amorphous and are compositionally broad and structurally diverse
3. Defects and or doping where substitutions or vacancies are tolerated to a certain level.

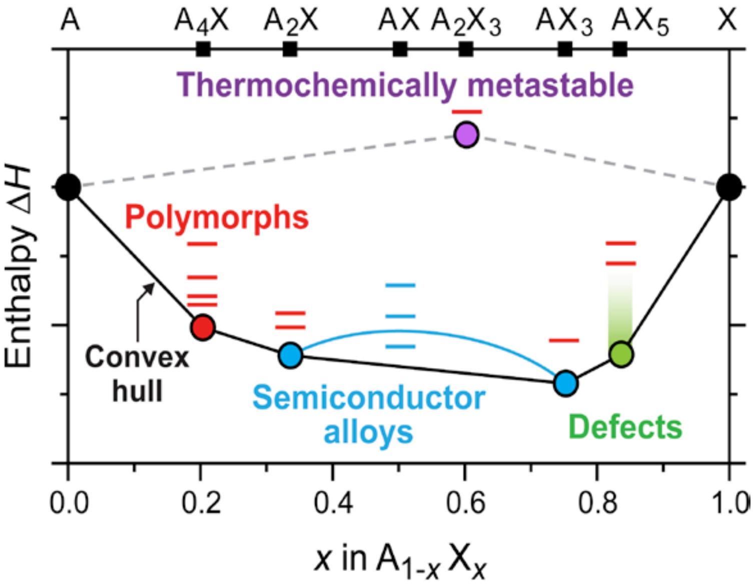

Figure 1 illustrates the primary four classes of metastable materials (shown in color) targeted for theory-driven synthesis in the CNGMD EFRC

Our initial work on metastability and synthesizability is aimed at developing high throughput theory and experimental tools to probe the manifold of polymorphs for specific metal oxide systems, VOx and MnOx, both of which have a rich literature on functional polymorphism and where polymorphs are accessible by a variety of synthetic tools. We will employ diverse synthetic approaches including solution-based, electrodeposition and physical vapor deposition processes. Key questions to be addressed are how can new polymorphs systems with functional materials be identified, how large an energy difference is needed to target the different polymorphs and can synthetic pathways be identified specific to a specific polymorphic system?

In the alloy area, we are working to predictive possible intermediate metastable structures and develop and specific synthetic paths to produce targeted functional materials. For defects and doping, we aim to develop the ability to predict the inherent defects in a new or existing materials as well as to identify potential substitutional or interstitial dopants. For many new materials dopability or the lack thereof is key to the functional application of the materials and the development of functional interfaces. Initial work is focused on understanding the ability to dope $Ga_3O_3$ an increasingly interesting material for buffer/contact layers in solar cells and the active element high power transistors. The work integrates the ability to predict defects, describe the electrical activity and identifying pathways to generating the metastable defect densities.

## Data Management and Open Access

Databases on materials properties, as well as methodologies for Materials by Design, will be made publically available. The EFRC database will also interact with the larger data sets already available in the Materials Project.

## Publications

In progress.

# Designing, Understanding and Functionalizing Novel Superconductors and Magnetic Derivatives

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**Keywords:** FeAs systems, magnetic semiconductors, MuSR, neutron scattering, electrolyte gating

## Project Scope

This project aims development, characterization, and functionalization of FeAs superconductors and the derivative ferromagnetic semiconductors obtained by replacing Fe with (Zn,Mn), LDA, DFT and DMFT calculations are used to obtain electronic structures and predict novel compounds with various compositions and constituents. These systems will be characterized by neutron scattering, muon spin relaxation and transport measurements. Modern synthesis techniques, micro-fabrication and electrolyte gating will be used to develop junction devices with new functionality. The results will be fed back to theoretical and computational materials designs. This method will also be applied to other superconductors and Mott-transition systems.

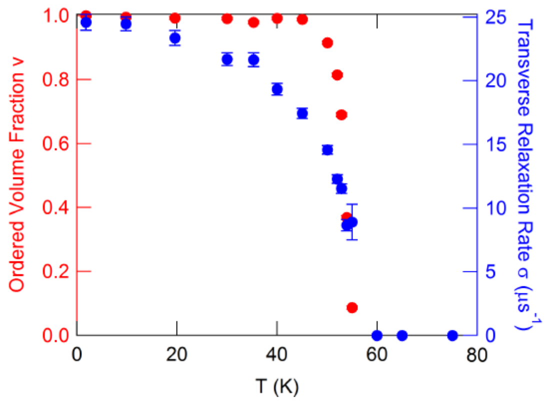

**Figure.** Muon spin relaxation (MuSR) results in zero field on assembled single crystal specimens of $(Ca_{0.73}La_{0.27})FeAs_2$. A sharp magnetic order at T~ 53 K is seen with full volume fraction of magnetically ordered state at lower temperatures. Smooth increase of the static local field parameter σ (blue points) indicate building up of magnetic order parameter consistent with second-order transition. (unpublished DMREF results)

## Relevance to MGI

Kotliar is a leading theorist who made seminal contributions to Dymanical Mean Field Theory (DMFT), He has used DMFT, LDA and other methods to predict superconducting (SC) and magnetic materials before synthesis, such as the 112 FeAs superconductor $BaFeAs_2$, later synthesized with SC $T_c$ = 45 K. He also predicted spin excitation results quantitatively comparable to inelastic neutron scattering results of Dai. These feedback processes will be further strengthened by additional activities on diluted ferromagnetic semiconductors, Mott transition systems, muon spin relaxation experiments (Uemura) , single crystal growth (Ni), and nano-scale device fabrication and electrolyte gating (Kim).

## Technical Progress and Future Plans.

Following Kotliar's proposal in 2009 on new "112" FeAs-based superconductor $BaFeAs_2$ [1], a superconducting compound $(Ca,La)FeAs_2$ was synthesized by Katayama et al. [2] in 2013. In the summer of 2014, Ni Ni fabricated single crystal specimens of $(Ca_{0.73}La_{0.27})FeAs_2$ and collaborated with Uemura at TRIUMF, Vancouver to examine its magnetic property by muon spin relaxation measurments, As shown in Figure 1, a very sharp magnetic order was found at T ~ 53 K, developing in the full volume fraction, in this non-superconducting compound. This establishes that the SC phase of the 112 FeAs superconductors appear adjacent to static magnetic order, similarly to other families of FeAs-based superconductors. Elastic neutron scattering studies are underway, and inelastic neutron studies will be performed by Dai and Ni, seeking nematic correlations.

Superconducting compounds of the 112 family are known to exhibit poor superconducting volume fraction in magnetic susceptibility measurements. The Ni group will seek improvements of materials quality, while collaborating with the DMREF group to elucidate promising superconducting properties in hydrostatic pressure.

Following combined neutron scattering (by Dai) and electronic structure calculation (by Kotliar) studies on spin fluctuations in electron-doped $Ba(Fe,Ni)_2As_2$ superconductors, the Dai group has started elastic and inelastic neutron studies on $BaFe_2(As,P)_2$ tuned by iso-valent substitution. Unlike quantum critical divergent effect stressed by other groups on the (As,P) system, recent studies of Dai by neutron and NMR revealed [3] weakly first-order evolution at the point where static magnetic order disappears. This feature is similar to the absence of quantum criticality revealed by MuSR (by Uemura) and neutron (by Dai) measurements on the electron-doped $Ba(Fe,Ni)_2As_2$ system. Combination of neutron and muon studies on the (As,P) system is underway by Dai and Uemura, while neutron studies will be extended to inelastic measurements and compared with Kotliar's calculations.

Ni and Kotliar have also worked on synthesis and band structure calculations of a poor metal $BaTi_{13}O_{12}$ [4].

## Future Plans

Diluted semiconductors, with ferromagnetic Curie temperature $T_C$~200 K and having a crystal structure identical to the 122 FeAs superconductors, have been developed by Uemura's PIRE collaboration [5]. Kim, Ni and Uemura will seek formation of junction devices with companion compounds obtained by substituting Fe with Zn and/or Mn. Kim and Uemura also started to collaborate on MuSR and transport studies of $(Sr,La)_2IrO_4$ elucidating Mott transitions. Such studies will be expanded to $V_2O_3$, in collaboration with Dimitri Basov who imaged microscopic phase separation by nano-optics and with Kotliar who performed electronic structure calculations [6].

## Broader impact

In 2011 with NSF PIRE support, the PI Uemura initiated Frontiers of Condensed Matter Physics (FCMP) lecture series for CMP graduate students, connecting remote classrooms by online simultaneous broadcast (simulcast) and archives of voice-synchronized videos, at Columbia, Rice, U. Tokyo and several Chinese institutions. Enrolled students joined subsequent foreign tours to meet with leading CMP lecturers and students from other schools who took the same course. With DMREF PI's, the fourth FCMP lectures have been organized in Fall-2014 semester connecting Columbia (35 enrolled), Rice (10), Harvard and CBPF-Rio-Brazil (online auditing). In May 2015, a Workshop will be held at an accelerator facility TRIUMF in Vancouver, so that DMREF PI's, other CMP leaders and FCMP students can obtain hands-on experiences of muon spin relaxation (MuSR) experiments and enjoy discussions on modern research topics. These activities help education of US students in international environment.

## Data Management and Open Access

The Kotiar group has already significant experience with data hosting, visualization of stored data, and archiving scientific data via a dedicated web-portal http://hauleweb.rutgers.edu/database_w2k/. All calculations which are published in scientific journals of DMFT sub-group are first saved into this database, such that other students and postdocs, as well as the scientific community at large, can download and reproduce them, and further analyze the results or compare to experimental data. MuSR data of Uemura will be made available to public via TRIUMF CMMS web site. Part of neutron data of Dai will be available via the above-mentioned Rutgers site.

## References

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# Design and fabrication of wide-band-gap nitride-based alloys

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**Keywords:** nitride semiconductors, defects, density functional theory, molecular beam epitaxy, deep level spectroscopy.

## Project Scope

The nitride semiconductors are driving solid-state lighting and will have a similarly high impact in power electronics. High-quality alloys with larger band gaps are required to push optoelectronics into the UV and to enable higher voltage transistors. Computational theory, in tight collaboration with growth and characterization, will accelerate the development of these materials by exploring suitable alloy compositions and heterostructures. Materials to be explored include AlN, Al-rich AlGaN and InAlN alloys, and BAlN. Detailed studies of the relationship between native defects, unintentional impurities, and doping will be performed. A new methodology for calculating capture cross sections will enable direct comparison with deep-level optical spectroscopy.

## Relevance to MGI

First-principles calculations based on cutting-edge theoretical techniques are being performed, yielding the most accurate description currently available at the system sizes needed for modeling defects and heterostructures. Topics to be addressed include band alignment, polarization properties, identification of suitable dopants, the role of unintentional impurities, and strategies for avoiding detrimental defects. Growth will be carried out by plasma-assisted molecular beam epitaxy (MBE) or ammonia MBE. Closing the loop between theory and experiment will provide deep understanding of fundamental atomic-level mechanisms and phenomena associated with synthesis and processing.

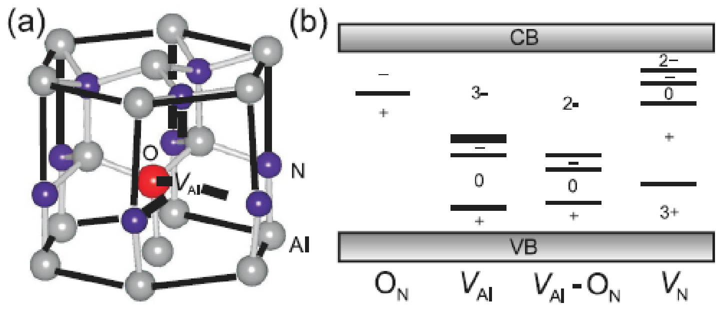

**Figure 1.** (a) Atomic structure of the $V_{Al}$-$O_N$ complex in AlN, calculated with hybreid density functional theory. (b) Thermodynamic transition levels obtained from defect formation energies. Conduction and valence bands are denoted by CB and VB.. From Ref. [1].

## Technical Progress

We are performing first-principles calculations based on density functional theory with a hybrid functional; this approach provides the most accurate description currently available at the system sizes needed for modeling defects and heterostructures. Atomic and electronic structure of alloys as well as their polarization properties are to be calculated and will guide growth. Deep and shallow levels of defects and impurities are being investigated and their impact on optical and electronic properties assessed. An example is shown in Fig. 1, which illustrates the atomic structure of a complex between an Al vacancy ($V_{Al}$) and a substutional oxygen impurity ($O_N$) in AlN. Calculated defect levels in the band gap for selected defects are shown in Fig. 1(b). These levels can be compared with cutting-edge experimental deep-level optical spectroscopy, which allows determination of defect levels throughout the band gap of wide-gap semiconductors.

High-quality epitaxial growth by MBE enables detailed characterization of interfaces, point defects, and impurities using structural, electrical, and optical techniques. *p*-type doping is a major challenge in Al-rich nitride alloys. *n*-type conductivity is also limited, since common donors such as O and Si tend to act as DX centers, leading to compensation and lowering of free-carrier concentration. Unintentional impurities act as deep traps and sources of luminescence in GaN, and likely behave similarly in Al-based alloys. Native defects are also expected to be more prevalent in the wide-band-gap nitrides, acting as compensating centers, nonradiative recombination centers, or sources of unwanted absorption or emission. The knowledge generated by the combined computational and experimental efforts is essential to enable the required degree of control over materials properties.

## Future Plans

We will also pursue an investigation of a largely unexplored novel alloy system, namely BAlN.

## Broader impact (Optional for DOE grants/FWPs)

We aim to have a strong impact on technology: the semiconductors at the focus of this investigation are prime candidates for the fabrication of UV light emitters and for novel transistors for high-power electronics. The development of compact UV light sources impacts a wide range of technologies, including photolithography, optical data storage, detection of hazardous particles, water or air purification, and sterilization. High-power electronics can lead to tremendous energy savings in power conversion. We are aiming to effectively communicating research results in publications, talks, and interactions with industry. Graduate students are being involved in a tight collaboration between theory and experiment, and a larger group will benefit from integration of the ongoing research in courses taught by the PIs and discussions in student seminars. We are also involving undergraduate students in their research, as well as their effort in broadening participation of underrepresented groups.

## Data Management and Open Access

The first-principles calculations are based on open-source as well as commercial codes. Band structures and formation energies are tabulated in spreadsheets. Raw and processed data is stored on long-term data storage (at supercomputer sites associated with the NSF-funded XSEDE as well as clusters at UCSB). Input and output files can be uploaded to NSF-supported ESTEST, a web-based framework for the sharing and comparing of electronic structure codes (http://eslab.ucdavis.edu/software/estest/index.htm).

In the UCSB MBE Laboratory, all growth runs are recorded either in an electronic database using Filemaker Pro, or in log books that are kept available for all growers and archived onsite. A cloud-based electronic log with easy search capability and advanced security capabilities is being developed. Data from defect spectroscopy is stored on file servers at OSU.

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# Integrated computational framework for designing dynamically controlled alloy-oxide heterostructures

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**Keywords:** Multi-scale, dynamically evolving heterostructures, oxidation, sensitivity analysis

## Project Scope

Our aim is to develop an infrastructure that integrates first-principles multi-scale computation with precise experimental characterization to predict the evolution of complex multi-phase structures. Such tools are crucial for the design of protective coatings, targeted microstructures for catalysis and electrochemical energy storage devices. We are developing this infrastructure in the context of the measurement and prediction of thermodynamic and kinetic properties of oxidation processes in model Ti-Al alloys. Experiment serves to benchmark, validate and iteratively improve multiscale descriptions that bridge first-principles statistical mechanical methods with phase field models and level set methods. A crucial component of this effort will be the development of sensitivity analysis tools for multi-scale simulation.

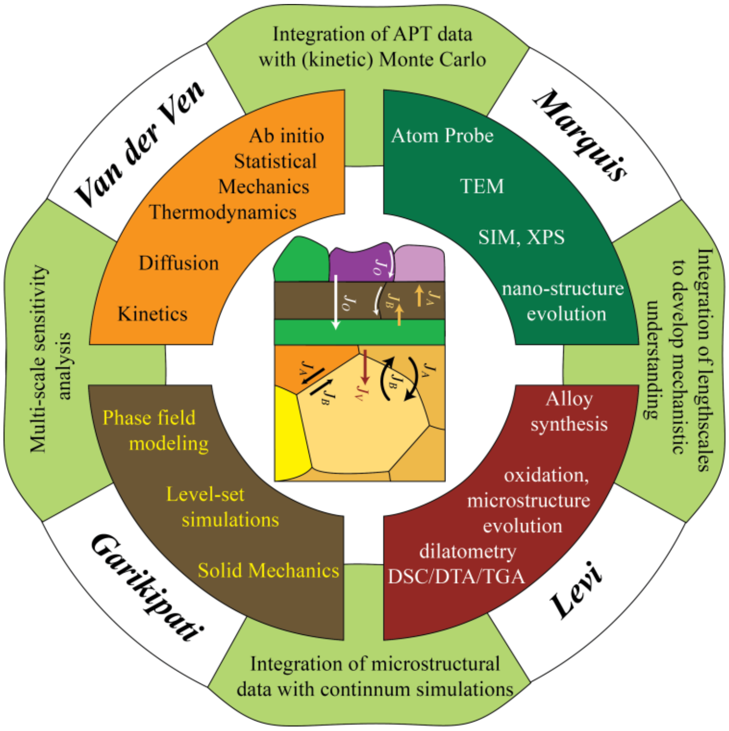

**Figure 1:** The prediction of the dynamic evolution of a multi-phase system, as during the oxidation of an alloy, requires a multi-scale approach that links first-principles statistical mechanical methods with continuum simulation tools. Many of the phenomenological laws for unit kinetic processes remain to be rigorously established. An iterative coupling with experiment, relying on sensitivity analysis tools, will lead to the establishment of a robust and rigorous theory of non-equilibrium processes as occur during oxidation, the synthesis of complex microstructures for catalysis and the working of electrochemical energy storage devices.

## Relevance to MGI

Even the most advanced first-principles statistical mechanical methods rely on a variety of approximations that are difficult to avoid. Experiment will remain crucial, not only to identify unsuspected behavior and phenomena, but also to parameterize constitutive thermodynamic, kinetic and mechanical properties. Our aim is to integrate first-principles methods with experiment to leverage the strengths of both to their fullest. To this end, we will develop sensitivity analysis tools to detect emergent behavior in the multi-scale models and to iteratively refine thermodynamic and kinetic descriptions to make them quantitatively consistent with experimental measurements. Targeted experimental measurements will be made of perturbed kinetic processes and internal parameters, and their influence will be tracked through the cascade of multi-scale models.

**Technical Progress**

Four months into the project, we have made Ti-Al samples for oxidation experiments, formulated sensitivity analysis methods for the multi-scale framework and developed a level set formalism and software to predict the migration of sharp interface due to coherency strain energy driving forces.

**Future Plans**

Our integrated infrastructure will be developed in the context of a study of the oxidation of high-purity binary Ti-Al alloys. We will develop methods and computational tools to link first-principles statistical mechanical methods with continuum phase field and level set approaches and integrate these tools with atom probe tomography (ATP) and electron microscopy measurements.

First-principles statistical mechanical techniques will be used to calculate the thermodynamic and transport properties of all phases that can form in the Ti-Al-O system. The statistical mechanical predictions will be tested and interfaced with ATP measurements on binary Ti-Al alloys and their oxides. Comparisons will be made between on the one hand experimentally measured short-range order parameters, diffuse interface thicknesses and coherent precipitate size and distribution and on the other hand results from kinetic Monte Carlo simulations and phase field simulations that rely on first-principles chemo-mechanical free energies and diffusion coefficients. The first-principles predicted thermodynamic descriptions will further be validated and quantitatively improved upon by comparing predicted phase stability to results from DSC/DTA/TGA measurements as well as solubilities measured in coexisting phases. The iterative improvements of the bulk phase thermodynamic and kinetic descriptions will be aided by sensitivity analysis tools to be developed within this project. Experimental and modeling students supported by the program will develop software to convert experimental APT data and other microstructural images into formats that interface with the Monte Carlo and continuum simulation tools

Microstructure evolution will be predicted by combining elementary constitutive properties within a three-dimensional continuum simulation framework that relies on phase field models and level-set methods. These simulations will be validated with experimental measurements of microstructure evolution. The continuum simulations will start from representative experimentally characterized microstructures. A key unknown at this stage are the interface and grain boundary response function with respect to their mobilities as well as their role in facilitating short-circuit diffusion for ions and electrons. These response functions will be iteratively parameterized by matching continuum predictions of microstructure evolution during oxidation with experimental observations. Sensitivity analyses with respect to mechanisms and kinetic rate laws will be applied to the continuum simulations to determine the relevance and correct form of different kinetic constitutive equations.

**Broader impact (Optional for DOE grants/FWPs)**

A major outcome of this work will be the formulation and implementation of a methodology and computational/experimental infrastructure that rapidly characterizes, elucidates and enables the design of heterostructures with desired properties as relevant to oxidation, corrosion, catalysis and electrochemical energy storage devices. The project will specifically fund three graduate students and one post doc who will be uniquely exposed to ICME techniques and the requisite interplay between experimental and theoretical research. The PI's will also participate in ICME related summer schools to educate a broader community of students about multi-scale modeling approaches

**Data Management and Open Access**

Software developed within this program will be made publically available. Software will also be developed to generate data in standard data base formats consistent with repositories that will be made accessible to the public (e.g. the DOE funded PRISMS materials commons repository at the University of Michigan).

# Enhanced functionalities in 5d transition-metal compounds from large spin-orbit coupling

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**Keywords:** 5d compounds, spin-orbit coupling, layered chalcogenides, $IrTe_2$.

## Project Scope

The physics and chemistry of 4d and 5d transition-metal compounds is distinguished by strong spin-orbit coupling, which can have a dramatic effect on materials properties. The focus of this DMREF project is to improve our scientific understanding of materials containing 5d elements and harness their unusual properties to develop new functional materials. Our goals include (i) achieving large magnetocrystalline anisotropy in crystals with mixed 3d and 4d/5d transition-metal ions; (ii) finding new topological insulators and materials with other novel topological band structures; (iii) demonstrating unusual superconducting states; and (iv) developing materials with giant magnetoelectric, multiferroic, or magneto-optic effects.

## Relevance to MGI

The project is a joint theoretical, computational, and experimental research effort built upon a materials discovery paradigm in which first-principles calculations are used to scan through candidate materials, identifying promising candidates for directed synthesis and in-depth experimental study. Comparisons between theory and experiment provide feedback to refocus the theoretical and computational effort. We seek a transformative acceleration of progress in our understanding of these materials, especially regarding the interplay between competing interactions that give rise to functional behavior.

## Technical Progress

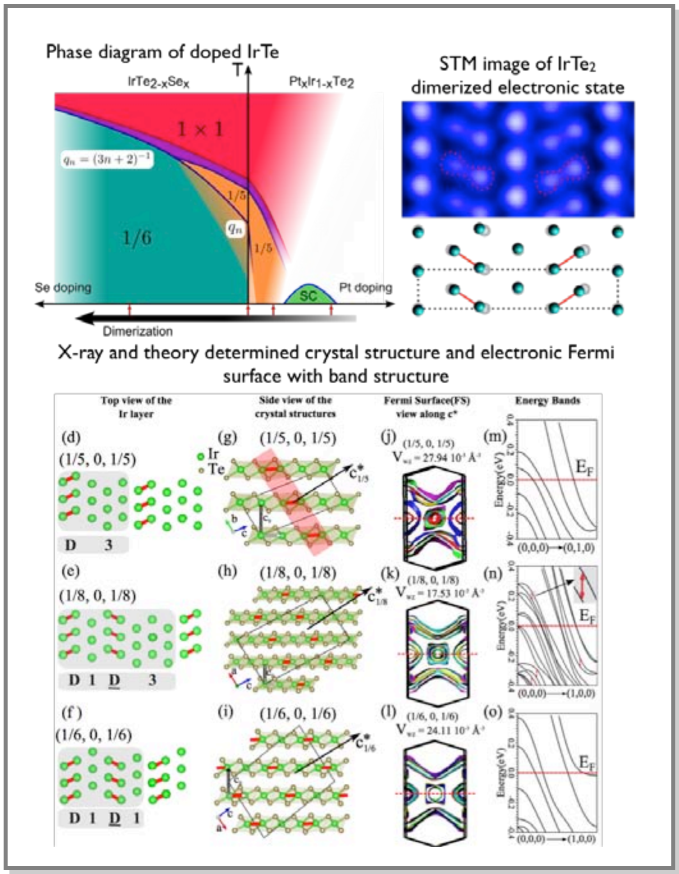
Our activity has been broad, with 10 papers published and 2 in press. Here we highlight just a few items.

$IrTe_2$ is a new exemplary material, where the strong spin-orbit coupling (SOC) associated with Ir and Te ions is associated with a multitude of structures that compete in energy, such that the compound can be tuned by strain, pressure, or doping to transform from one state to another. Some of these structures lack inversion symmetry, and when combined with large SOC, this leads to spin-polarized bands, a property that can be used in spintronics applications. The Rutgers-Tennessee DMREF team has theoretically predicted the existence of exotic states with spin-polarized bands, and also confirmed and characterized them using X-ray, optical, scanning-tunneling, quantum-oscillation, and neutron-scattering techniques [Pubs. 2, 4-6, 9-10, 12, 14; see figure next page].

We extended dynamical mean-field theory (DMFT), a well-known tool for treating strong correlations, by adding the capability to treat strong SOC, thereby providing for the first time a practical theoretical tool for investigating competing orders in strong spin-orbit materials. We initially applied the new technique to study the Ruddlesden-Popper series of strontium iridates and related materials, showing how single-particle spectra, optical conductivities, and orbital and spin moments change with strain, and we demonstrate that the ground state can be well characterized in terms of a modified effective energy-dependent $J_{\mathrm{eff}}$=1/2 state [Pub. 13].

We discovered that $Ni_3TeO_6$ exhibits a colossal magnetoelectric effect, the largest known to date, arising from a non-hysteretic spin-flop transition separating the antiferromagnetic and weak-ferromagnetic phases, and extending to remarkably high frequencies. We predicted theoretically that a soft magnon mode in the vicinity of the magnetic critical point and a high-order magnetic anisotropy are responsible for this unique effect [Pubs. 1, 11].

We explored an ionic Field Effect Transistor (iFET) in layered 1T-$TaS_2$ using ionic gating. We found that the fast and reproducible iFET effect is mostly due to fast diffusion of Li ions [Pub. 3].



### Future Plans

Materials with strong 5*d*-shell SOC and correlations are promising candidates in the search for novel topological phases including topological Mott insulators, axion insulators, and Weyl semimetals. Such phases have been suggested to occur in pyrochlore iridates, but a realistic ab-initio study has been unavailable. We will investigate $Ln_2Ir_2O_7$ pyrochlore iridates using our new SOC-capable version of DMFT, which correctly predicts the existence of the metal-insulator transition with increasing Ln radius. We will carry out a materials-specific determination of exotic phases in this class of materials, supported by materials synthesis and characterization that will be undertaken for materials predicted by our theory to harbor exotic phases. We will also explore the large magnetocrystalline anisotropy of the $J_{\mathrm{eff}}$=1/2 state of octahedrally coordinated $Ir^{4+}$ in different local environments, e.g., in double perovskite $R_2CuIrO_6$ (R=rare earths) and the chain magnets of $Sr_3IrIrO_6$ and $Sr_3IrPtO_6$. We also plan to predict and synthesize superlattices of $Bi_2Se_3$ and $TMSe_2$ (TM=Nb, Mo, Ta and W), which are expected to have novel metal-insulator and topological superconducting transitions.

### Broader impacts

We will continue to provide research experience for high school students during summers through the Partners in Science Program of the NJ Liberty Science Center, and for undergraduate students though the Rutgers REU (Research Experience for Undergraduates) program and the Aresty program. We have advanced our field through workshops/conferences that we have organized, notably the 2013 and 2015 *Telluride Workshops on Spin-Orbit Coupling in 4- and 5d-Containing Materials*, and the *2014 Gordon Research Conference (GRC) on Multiferroic and Magnetoelectric Materials*. The GRC provided for the involvement of grad students, postdocs, and young researchers. We also initiated a new *Focused Topic on Strongly Spin-Orbit Coupled Materials* starting with the 2015 March APS meeting, which will foster interactions between junior and senior researchers.

### Data Management and Open Access

Our publication list, published papers, and other materials are posted on our DMREF project webpage http://dmref.physics.rutgers.edu. General data are stored at http://hauleweb.rutgers.edu/database_w2k/, and codes are available at: http://hauleweb.rutgers.edu/tutorials/.

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# In Silico Prediction of Catalytic Materials for Biomass Upgrade in the Catalysis Center for Energy Innovation

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**Keywords:** Biomass, heterogeneous catalysis, zeolites, metals, multiscale modeling

## Project Scope

Within CCEI, our objective is to develop multifunctional, hierarchical (with porosity extending over multiple scales), hydrothermally stable, active and selective catalytic materials to enable the complex transformation of biomass to fuels and chemicals in complex media. Supports include zirconia, titania, carbon, and zeolites. Functionalities engrafted on these supports include combinations of Brønsted and Lewis acidity along with single and core-shell metal sites. We develop multiscale models and first-principles-based semi-empirical methods for rapid screening of materials. The model predictions are assessed experimentally in catalytic experiments.

## Relevance to MGI

Within each research thrust, we integrate model prediction, materials synthesis and characterization, and catalyst evaluation along with spectroscopy in full alignment with the MGI scope. Due to the multiscale nature of catalytic processes and the inherent complexity of reaction mechanisms, we often start with experimentally assessing a kinetic model followed with in silico prediction of materials, synthesis and evaluation.

## Technical Progress

We have demonstrated in silico prediction of materials in several instances, such as in reforming and hydrodeoxygenation of biomass by proposing suitable core-shell bimetallics and carbide catalysts. We also proposed functionalities for para-xylene production using Lewis and Brønsted acid based materials.

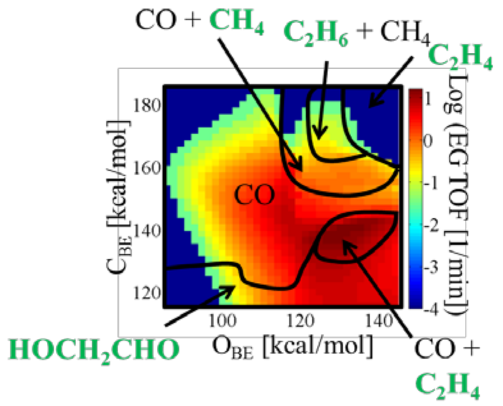

**Figure 1.** Prediction of catalyst activity and selectivity for ethylene glycol vs. binding energies of C and O. Matching of optimal properties with those of various core-shell structures provides in silico prediction of novel materials that can be assessed experimentally.

## Future Plans

Despite the significant progress made today, we are still working on developing design principles for several classes of multifunctional materials.

## Broader impact (Optional for DOE grants/FWPs)

We educate graduate students and postdocs in an interdisciplinary, team-based environment where experimentalists and modelers work side by side and interact with multiple faculty. In addition, we provide short courses and a rotational program whereby students can visit other institutions. Finally, we hold an REU program for undergraduates.

## Data Management and Open Access

We develop thermochemistry, quantum mechanical models, and kinetic models, and provide these in peer review publications and through our web site for download.

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# Materials Modeling in the Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME)

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**Keywords:** acid gases, MOFs, porous carbons, catalysts

## Project Scope

The Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME) is a DOE Energy Frontier Research Center that began in August 2014. The Center focuses on fundamental questions associated with understanding and mitigating evolution of high surface area porous materials and heterogeneous catalysts in environments that include acid gases. Close interaction between experimental and modeling efforts is being used to study a range of materials to allow broadly applicable knowledge to be generated associated with the effects of acid gases on materials.

## Relevance to MGI

Each of the Center's four Thrusts includes direct connections between experimental and modeling efforts, and modeling efforts within the Center are being coordinated among Thrusts to maximize the impact of these crosscutting activities. Computational techniques being used include high level quantum chemistry, plane wave Density Functional Theory, classical and reactive force fields.

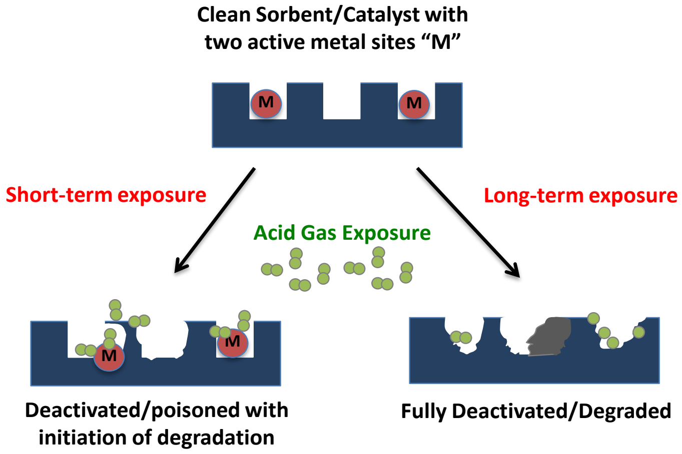

**Figure 1:** Changes induced in sorbents/catalysts upon short- and long-term exposure to acid gases. Materials are typically treated as passive in these environments, but can change dramatically upon exposure to $SO_x$, $NO_x$, and $H_2S$.

## Technical Progress

The Center began in August 2014, and includes a strong core of computational modeling, with participation from David Sholl (Georgia Tech, EFRC Deputy Director), Tjerk Straatsma (ORNL), Bobby Sumpter (ORNL), David Dixon (University of Alabama), Susan Sinnott (University of Florida), and JR Schmidt (University of Wisconsin). The Center is organized into four interrelated Thrusts. Thrust 1 (led by Zili Wu, ORNL) focuses on acid-gas interactions with model oxide-based surfaces and supported oxides. Thrust 2 (led by Sankar Nair, Georgia Tech) focuses on defects in high surface area porous materials such as metal-organic frameworks (MOFs), and will use modeling as a key approach to interrogate these defects. Thrust 3 (led by Christopher Jones, Georgia Tech) focuses on crystallographically disordered porous materials such as supported amines and carbide-derived carbons. Modeling will be used in this Thrust in close conjunction with characterization using NMR and other experimental methods. Thrust 4 (led by David Sholl, Georgia Tech) focuses on the external surfaces of ordered porous materials such as MOFs, both in the form of external surfaces of porous particles and 2D analogues of these materials grown on controlled planar substrates.

**Future Plans**

The four major research goals of the Center are to:

1. Develop a deep knowledge base characterizing acid gas interactions applicable to a broad class of materials.
2. Develop fundamental knowledge allowing practical predictions of materials interacting with complex gas environments on long time scales.
3. Advance fundamental understanding of the characterization and control of defects in porous sorbents.
4. Accelerate materials discovery for large-scale energy applications by establishing broadly applicable strategies to extend material stability and lifetime in the presence of acid gases.

**Data Management and Open Access**

Computational efforts within the Center examining crystallographically ordered porous materials are being coordinated with efforts with the DOE-funded Nanoporous Materials Genome Center (NGMC), and data management of structures developed within UNCAGE-ME will be distributed using the tools being developed by the NGMC. Other data sets will be made available via the UNCAGE-ME website (efrc.gatech.edu) as appropriate.

# Accelerated Development of Next Generation Ti Alloys by ICMSE Exploitation of Non-Conventional Transformation Pathways

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**Keywords:** Ultrafine microstructure, Texture-free, Spinodal, Pseudo-spinodal, Heterogeneous nucleation

## Project Scope

This DMREF program builds on our discovery of non-conventional transformation pathways (DMR1309270) to design new Ti-alloys with ultrafine $\alpha+\beta$ microstructures. The scope is to *accelerate* the realization and utilization of the *new transformation pathways* and revolutionary alloy design concepts in the development of next generation Ti-alloys, by integrating multi-scale computational modeling and simulation with critical experimental characterization involving combinatorial approaches based on rapid prototyping. Ultrafine and uniform microstructures with little or no micro-texture are expected from the new transformation pathways and substantially improved properties, e.g., an excellent combination of strength and ductility and high temperature microstructural stability, are anticipated.

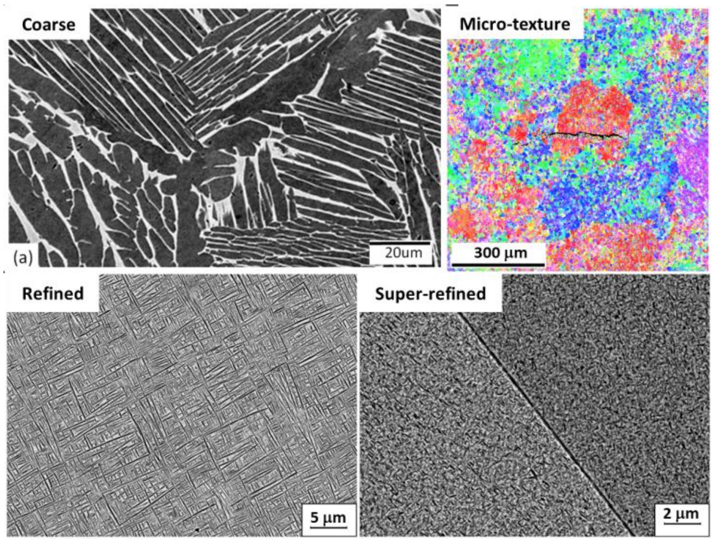

**Figure 1.** *Top*: Typical α + β microstructures and transformation texture in Ti-alloys produced through the conventional transformation pathways (TPs); *Bottom*: Refined and super-refined α + β microstructures produced via non-conventional TPs.

## Relevance to MGI

Using available CALPHAD free-energy databases for the $\alpha$ and $\beta$ phases in Ti-Mo and Ti-Mo-Al alloys, miscibility gaps and $T_0(C_0)$ are first predicted. Phase-field simulations are then carried out to predict microstructure evolution along precursory-spinodal and pseudo-spinodal transformation pathways. Ab initio calculations and high temperature synchrotron experiment are being/will be carried out to validate CALPHAD predictions and SEM/TEM/APT characterizations are being carried out to validate the microstructures as function of time-temperature and alloy composition predicted by the phase-field simulations. The new data will be integrated into the CALPHAD database, initiating the next iteration of the integrated program till fast prototyping.

## Technical Progress

*(a) Precursory phase separation via spinodal decomposition*

Both experimental observations and simulation predictions have demonstrated that the pseudo-spinodal mechanism does offer a new way to produce ultrafine and uniform $\alpha+\beta$ microstructures in-Ti alloys. However the processing window for this mechanism to operate is rather narrow. The free-energy model currently available in PANDAT databases for the $\beta$ phase in Ti-Mo shows the existence of a miscibility gap, which provides a new opportunity to design a non-conventional transformation pathway, i.e., precursory phase separation by spinodal decomposition (precursory-spinodal), to engineer ultrafine $\alpha+\ \beta$ microstructures in much wider composition and temperature ranges. Our simulation results have confirmed this possibility and our experimental observations have shown that refined $\alpha+\beta$ microstructures can be obtained in a wide composition range in Ti-Mo.

*(b) $\omega$-assisted $\alpha$ nucleation and growth*

In our on-going experimental study (DMR1309270) of heating rate effects on athermal ω → isothermal ω transformation and its effect on intragranular α nucleation in Ti-5Al-5Mo-5V-3Cr and TIMETAL 21S alloys, even finer $\alpha + \beta$ microstructures called super-refined $\alpha + \beta$ microstructures (Fig. 1) have been obtained. In this program effects of ω precipitation on α nucleation have been studied systematically using phase-field simulation and the results are guiding new experiments. Currently, this mechanism is being explored in Ti-Mo, Ti-Mo-Al and Ti-V systems. Characterization tools such as TEM, HAADF-HRSTEM and 3DAP have been employed to study critical issues related to how $\omega$ assistes intragranular α precipitation.

*(c) Mechanical property testing of ultrafine $\alpha + \beta$ microstructures*

Preliminary microhardness tests from Ti-5553 and room temperature tensile tests on the TIMETAL 21S alloy, both containing ultra-refined $\alpha$ precipitates, show substantial enhancements in their mechanical strength.

## Future Plan

*(a) Confirmation and utilization of precursory-spinodal mechanism*

- To determine further either precursory-spinodal or pseudo-spinodal mechanism operates in the model alloy systems, we will use *high temperature high-energy x-ray diffraction in the synchrotron* to investigate *in situ* phase separation before $\alpha$ precipitation. This study will be coupled with more detailed post-mortem characterization of microstructures formed along the transformation pathway using HAADF-STEM and APT. The detailed outcomes coupled with experimentally determined phase and crystallographic data will be used as critical inputs to the thermodynamic modeling and atomistic and phase-field simulations.
- Concentration modulation within the $\beta$ phase on activation energy and critical nucleus configuration of intragranular nucleation of $\alpha$ and the scale of $\alpha + \beta$ microstructure will be investigated using a combination of nudged-elastic-band (NEB) method and phase-field method.

*(b) $\omega$-assisted $\alpha$ nucleation and growth*

- Crystallography of $\beta \rightarrow \omega$ transformation including orientation relationship, lattice correspondence and defect structures at $\omega/\beta$ interface as a function of lattice parameters of the two phases and precipitate size will be investigated using experimental characterization and O-lattice and topological theories.
- Cluster expansion and NEB methods based on *ab initio* energetics have been used to formulate the free energy surface as a function of both concentration and displacement for the $\beta$-$\omega$ transformation in Ti-Mo. Such a free energy surface will be superimposed with that of equilibrium $\beta$ phase and used as input to phase-field to study the transformation pathway between $\beta$ and $\omega$ phases, in particular, the nucleation of athermal $\omega$ particles, their transition to isothermal $\omega$ particles, and the growth of isothermal $\omega$ particle.
- The effects of stress and concentration fields associated with $\omega$ precipitates on $\alpha$ nucleation will be investigated quantitatively using the NEB and phase-field methods. Experimentally characterized gradients in structure and concentration across interfaces will be used to determine the gradient energy coefficients used in the phase-field model.

## Broader Impact

The proposed program will directly prepare graduate students to immediately contribute to the success of ICMSE in industry. Additionally, the proposed training programs for researchers involved in materials development will afford a rapid uptake of the new methodology, resulting in very much increased effectiveness of our materials technologists. The computational tools and testing/verification data sets (fitted atomic potentials, amended thermodynamic functions, free energy surfaces, activation energy profile and configurations, generalized stacking fault energy surfaces, elastic constants, etc.) will be made freely available to industry and general public.

## Data Management and Open Access

To coordinate and manage data for the entire project, we will use web-based tool DMP Online (http://dmponline.dcc.ac.uk/), where we will build and edit a customized plan complying to NSF requirements. The atomic potentials developed will be archived at the NIST Interatomic Potentials Repository Project for other researchers to access and download. An instructional module will be uploaded at the NSF funded NanoHub portal at Purdue University. We are committed to making the computational tools and testing & verification data sets freely available to research community.

## Publications

D. Qiu, R. Shi, D. Zhang, W. J. Lu, and Y. Wang, “*Variant selection by dislocations during α precipitation in α/β titanium alloys*,” Acta Materialia (2014-Accepted).

# Emergent Functionalities at the Epitaxial Interfaces of Correlated and Spin-Orbit Materials

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**Keywords:** epitaxy, strain, proximity effects, superconductivity, topological insulators

## Project Scope

This project combines analytic and predictive computational theory with experimental epitaxial growth and atomic scale characterization to investigate the physical phenomena of thin materials on the order of one to a few unit cells that have enhanced functionalities emerging from the interplay of strain, proximity to the substrate, correlations, and spin-orbit interactions.

## Relevance to MGI

Density functional theory (DFT) calculations give the basic structural and electronic properties for model systems, allow the systematic variation of structural and composition parameters, and provide the basis and crucial interactions for many-body models of phenomena such as superconductivity. Samples of candidate systems, such as the Bi-bilayer films discussed below, are synthesized using molecular beam epitaxy, and then characterized *in situ* by atomic-resolution scanning tunneling microscopy/spectroscopy (STM/STS) as part of the iterative feedback loop of synthesis, characterization, and theoretical modeling.

## Technical Progress

The existence of edge/surface states of a topological insulator (TI) are a bulk symmetry property, but strain-induced changes in the bands may destroy the TI character. A free-standing (bi)layer of Bi at its bulk in-plane lattice constant is a TI, but calculations show a transition from insulating to semimetallic behavior for in-plane compressive strains of ~8% (c.f., Fig. 1a). A free-standing layer, however, is not realizable experi-mentally since thin TI films deposited on a substrate often have an epitaxial relationship in the initial stages of growth, the use of different substrates provides a means to strain engineer topo-logical phases. We have experi-mentally demonstrated this by epitaxially growing Bi bilayer films on three substrates with contracted in-plane lattice para-meters com-pared to bulk Bi: the (0001) surfaces of $Bi_2Se_3$ (8.8%), $Sb_2Te_3$ (6.4%), and $Bi_2Te_3$ (3.5%). Bi on the MBE samples forms epitaxial islands (Fig. 1b) on all three substrates, with the separation to the substrate increas-ing with the larger contraction. Spatially-resolved STS reveals protected 1-D edge states for strains below 8%, demonstrating strain engineering of topological phase transitions.

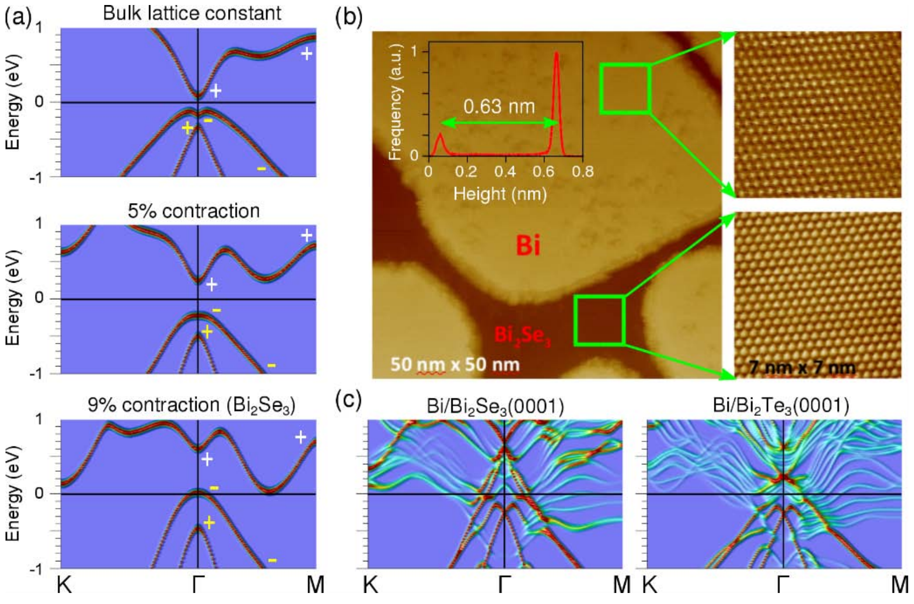

Fig. 1. (a) Calculated bands for single Bi bilayers at the bulk Bi lattice constant, for a 5% contract, and 9%, corresponding to the structure on $Bi_2Se_3$(0001). The parity of the states at the TRIM points are given. (b) STM images of single Bi bilayers on $Bi_2Se_3$(0001), with expanded views of the boxed regions. The inset gives the height distribution of the islands. (c) Bi bands for Bi on $Bi_2Se_3$(0001) and $Bi_2Te_3$(0001).

The Bi-substrate interactions, while small because of the weak (van der Waals) bonding, are not negligible, determining both the separation between the film and the substrate and the dispersion of the bands around the Fermi level.

For the case of the $Bi_2Se_3(0001)$ substrate, the calculated Bi bands (Fig. 1c) show a metallic behavior even more pronounced than for the free-standing Bi, while for the $Bi_2Te_3(0001)$ substrate, the Bi bands are effectively insulating, and thus able to support the TI edge states.

Pair density wave (PWD) superconductivity, where Cooper pairs have a finite center of mass momentum, has emerged as a viable explanation for anomalous properties of the pseudogap regime of the cuprates such as charge density wave order, superconducting fluctuations, and anomalous quasi-particle properties measured by angle resolved photo emission spectroscopy (ARPES). We have shown that PDW superconductivity can also account for signatures of broken time-reversal symmetry seen in the pseudogap phase and for the observed checkerboard charge density wave (CDW) order in *d*-wave superconductor vortex cores, and emerges as a degenerate ground state with CDW order in the spin-fermion model of the cuprates.

Electric field induced magnetism in itinerant transition-metals offer a new path to control magnetism at the nanoscale with ultralow energy power consumption. We investigated the change in the Curie temperature for an Fe monolayer and Co/Pt(111) by calculating the change in magnon (spin-spiral formation) energy in an external field. The field-induced screening charge in the spin-spiral states due to *p-d* hybridization modifies the Heisenberg exchange parameters and the magnetocrystalline anisotropy. The resulting change in $T_C$ suggest the possibility of tailoring magnetic properties by combining thin overlayer systems and external electric fields.

## Future Plans

The investigations of the TI-normal transition will be extended to other layered compounds such as Sb, increasing number of Bi layers, and the role of Fermi surface nesting features in altering the electronic structure by, for example, the formation of charge density waves.

Our DFT and ARPES studies of $Fe_2TeSe$ have demonstrated the importance of spin-orbit coupling and magnetism in determining the electronic structure of states around the Fermi level. We will investigate models of superconductivity in ultrathin layers of FeSe and related materials, where the substrate breaks breaks inversion symmetry leading to a spin-orbit coupling that can give rise to Cooper pairs that are a mixture of spin-singlet and spin-triplet components. The resultant gap function then has two contributions, resulting in two superconducting gaps instead of the usual single gap in the bulk. The focus will be on the changes induced in the superconducting layer by the substrate (e.g., by direct bonding, internal/external electric fields, and doping) using both DFT and model calculations. Promising substrate candidates beyond $SrTiO_3$ will be identified to facilitate epitaxial growth

## Broader Impact

All the graduate students and post-docs gain an understanding of different techniques, both in theory (computational density functional calculations and analytic many-body theory), and in the experimental aspects of molecular beam epitaxy growth and atomic-scale characterization. Undergraduates also have been involved in research; for example, Drew Melchert, an undergraduate from the U. Chicago spent the summer of 2014 with Agterberg working on PWD superconductivity and is a co-author on a manuscript posted on arXiv.

A physics teacher, Sarah Richter from Nicolet High School in Glendale, WI, spent 4 weeks in the summer of 2014 in Li's laboratory, providing her with exposure to the new materials-by-design paradigm: “Lego on the Atomic Scale”, by assembling single atomic layers like Lego blocks to synthesize novel materials with properties and functionalities beyond those exist in nature.

On the international outreach front, Weinert presented 3-day workshop on density functional theory and the relationship to real systems and experiments at the Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) in Bangalore, India in May 2014. Of the 50+ graduate students and post-docs, approximately half of the participants were women. In addition, a graduate student, Kenji Nawa, from Mie University (Japan) spent a month working with Weinert.

## Data Management and Open Access

An implementation of the Full-potential Linearized Augmented Plane Wave (FLAPW), *flair*, is actively being developed by the PI and an international group of collaborators, and is also being used by a number of other researchers worldwide. Much of the development is focused on approaches to allow more direct comparisons to various experimental probes, particularly spectroscopies. Some of these analysis tools have been ported and are available for other electronic structure codes, including *vasp* and *Quantum Espresso*.

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# Strong Correlation, DMRG and DFT

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**Keywords:** DMRG, DFT, Strong Correlation.

### Project Scope

Moderately and strongly correlated materials are at the heart of modern materials development. The goal of this project is to develop new algorithms and software to facilitate modeling of the most difficult new materials. This project combines two of the most important algorithms, the density matrix renormalization group and density functional methods, to improve the performance of each approach. These two approaches are being combined in a set of one dimensional benchmark systems of pseudosolids, where DMRG gives exact results even for hundreds of electrons, but which mimic the physics of strong correlation found in real materials. These results are used to understand DFT limitations and convergence; to benchmark improved DFT functionals; to test and improve hybrid DFT+DMFT/DMET methods, and provide training sets for developing machine learning functionals.

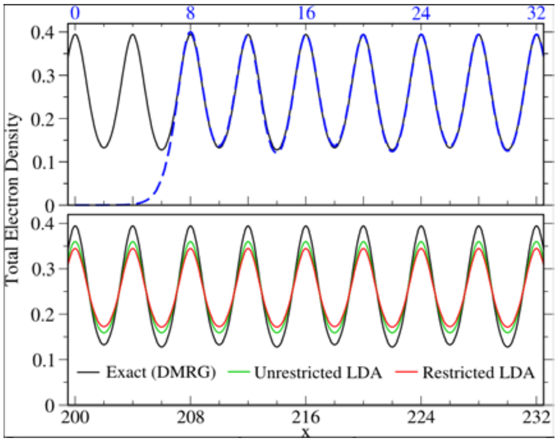

**Figure.** Central portion of a 100-atom 1D pseudosolid model system, where we compare the exact results from DMRG with restricted and unrestricted LDA approximations.

### Relevance to MGI

Our approach encompasses a close feedback loop between approximate but highly efficient DFT methods with expensive but highly accurate DMRG methods. DFT approximations are very difficult to evaluate in detail in realistic large 3D systems. By going to a 1D world, we can understand what can go wrong in fine detail in order to improve approximations. The project is producing DMRG-related algorithms and software, available publicly as part of the ITensor library at http://itensor.org. DFT functionals and model systems, as well as new theorems about the performance of DFT, are being published in scientific journals.

### Technical Progress

Progress has been made on several fronts: 1) DMRG for 1D pseudosolids: the 1D systems for which DMRG was developed were lattice systems rather than the continuum, and allowed only short-ranged (e.g. near-neighbor) Coulomb interactions. We have devised algorithms which allow the treatment of up to hundreds of electrons, in the continuum, with long-ranged interactions, with accuracies at the sub-millihartree level. 2) Pseudo-solid and pseudo-molecule models and benchmarks: we have developed and benchmarked model systems, showing that the types of correlation; the magnitude of correlation energies; and the overall qualitative behavior mimics that of realistic 3D strongly correlated systems. We have simulated the “electron gas” versions of these (with DMRG) to obtain exchange-correlation energies for use in LDA and related local functionals. 3) Understanding Convergence of Kohn-Sham algorithms in DFT: We have studied in detail the convergence of the standard Kohn-Sham algorithm as a function of the degree of strong correlation. In real materials, sometimes DFT calculations cannot be converged. One does not know whether this is due to the specific algorithms, to the approximate functionals, or a more fundamental limitation of DFT. However, motivated by our numerical results, we were able to prove analytically (and for 3D) that if one uses the simplest Kohn Sham convergence algorithm with the exact functional, the DFT will always converge--although the convergence can become exceptionally slow as correlations become stronger and gaps become smaller.

### Future Plans

One of the weaknesses of DFT methods is in obtaining gaps. We are well along in a project to study the behavior of gaps in our pseudosolid systems, both exact gaps and within DFT approximations. The DFT approximations include both the Kohn-Sham gap using the one particle LDA energy levels and the gaps obtained by changing the overall number of electrons in a finite system, and within both restricted and unrestricted versions of LDA. We are studying these as a function of system size and extrapolating to the thermodynamic limit. We hope to lay out guidelines for the best gaps available within the limitations of local DFT methods.

We are initiating a new machine learning project where we create a density functional by training over a large set of exact DMRG results for kinetic and total energies. If a functional can be obtained for the kinetic energy, this approach will eliminate the need for orbital-based (Kohn-Sham) algorithms, allowing scaling to very large numbers of atoms, with improved scaling in the number of atoms. This project would be too difficult to develop directly in 3D; in our 1D pseudosolid world it looks very promising. We have started initially just training for the kinetic energy, but we are transitioning to the full correlated energy.

Hybrid DFT/DMFT methods have been very important in the last decade, and a new alternative to DMFT, called DMET, is proving very effective in models and might be combined with DFT. Yet these approaches are not understood as well as one would like (e.g. issues of double counting); this makes these hybrids ideal for study in our pseudoatom systems. We hope to initiate a project in this area soon.

### Data Management and Open Access

Our key codes are being made available with free public access through the ITensor library, which is partly supported by this project. (See http://itensor.org). We are actively working to enhance the capability of this library, and to improve its ease of use and documentation.

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# High Efficiency Hierarchical Thermoelectric Composites by Multiscale Materials Design and Development

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**Keywords:** Thermoelectric Composites, hierarchical chemical bonding, Rashba effect, part-crystalline part-liquid state, core–shell composite model.

## Project Scope

We have studied the effects of Se-doping and fullerene coating on thermoelectric properties of $Bi_2Te_3$-based nanocomposites. Thermoelectric properties of materials with atomic level inhomogeneities have been investigated including the large Rashba effect in BiTeI, the electron-deficient II-V semiconductor CdSb, and part-crystalline part-liquid state in $Cu_3SbSe_3$, all of which show beneficial effect. Theoretical analysis of the effective behavior of core-shell composite show that higher thermoelectric conversion efficiency can be achieved in core–shell composites, and the mechanism responsible for the enhanced conversion efficiency is identified. Our continuum model tools have been experimentally validated in PbTe matrix that contains $Sb_2Te_3$ precipitates.

## Relevance to MGI

Our continuum model on thermoelectric composites identifies the optimal volume fraction and geometrical parameters for achieving high thermoelectric figures of merit. The experimental syntheses have been targeting the guidelines provided by the modeling.

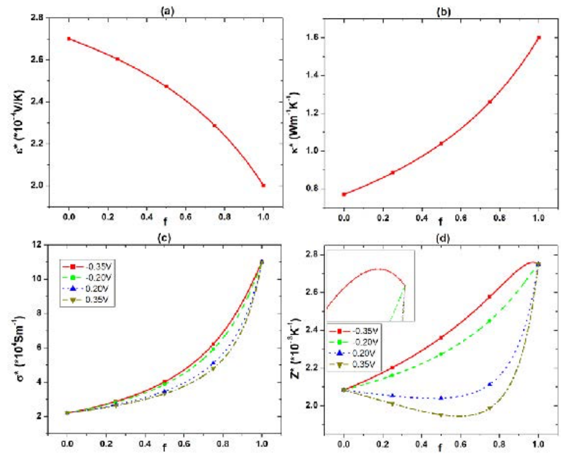

**Figure 1.** The effective Seebeck coefficient, thermal conductivity, electric conductivity, and figure of merit as functions of volume fraction for composite thermoelectrics.

## Technical Progress

The project has been focusing on (a) the understanding of atomic level chemical bonding inhomogeneity on electron and phonon transport of narrow gap semiconductors; (b) design, synthesis, and measurement of nanocomposite thermoelectrics; as well as (c) the development of a nonlinear asymptotic homogenization theory to analyze the effective behavior of thermoelectric composite with coupled transport of electricity and heat.

In the first example, we have demonstrated that anisotropic multicenter bonding in electron-poor II-V semiconductor CdSb is essential to both electrical and thermal transport. The anisotropic multicenter bonding leads to relatively high carrier weighted mobility and power factor, as well as intrinsically low lattice thermal conductivity, approaching the glass-limit at elevated temperatures. A maximum thermoelectric figure of merit ZT of ~ 1.3 at 560 K and an average ZT of 1.0 between 300 K and 600 K are achieved for the 0.5 at.% Ag-doped sample, making CdSb an attractive candidate for low-intermediate temperature or multistage power generations [1].

By analyzing the finite-temperature structural and vibrational characteristics of typical thermoelectric compounds such as filled skutterudites and $Cu_3SbSe_3$, we demonstrate a concept of part-crystalline part-liquid state in the compounds with chemical bond hierarchy, and thus rattling-like thermal damping due to the collective soft-mode vibrations similar to the Boson peak in amorphous materials. The observed abnormal lattice thermal conductivity close to the amorphous limit in these materials can only be described by an effective approach that approximately treats the rattling-like damping as a “resonant” phonon scattering [2].

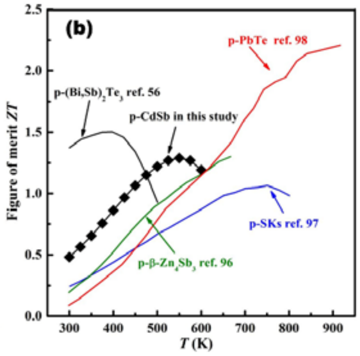

**Figure 2.** Comparisons of the best *ZT* in CdSb with those of somestate-of-the-art thermoelectric materials.

By using bulk BiTeI with a giant Rashba effect as an example, we prove that the spin-splitting-induced constant density of states leads to a two-dimensional thermopower. The thermopower is higher as compared with that in spin-degenerate bands, primarily due to the lower Fermi level in the Rashba spin-splitting bands at given carrier concentrations. A quantitative relation between thermopower and the Rashba parameter is established. Furthermore, the internal electric field in the Rashba system can be beneficial to bond anharmonicity and low lattice thermal conductivity. We suggest that bulk materials with large Rashba effect may become potential candidates for efficient thermoelectricity [3, 4].

We have also studied the effects of Se-doping and fullerene coating on thermoelectric properties of $Bi_2Te_3$-based nanocomposites. While Se-doping is beneficial mainly via the reduction of lattice thermal conductivity of the nanocomposites, fullerene coating seems to be detrimental.

Theoretical analysis of the effective behavior of core-shell composite show that higher thermoelectric conversion efficiency can be achieved in core–shell composites, and the mechanism responsible for the enhanced conversion efficiency is identified [5].

### Future Plans

In Future work will be focused on mitigate interfacial charge carrier scattering through doping the fullerene to decrease the energy barrier height across the interfaces in thermoelectric composites. Thermoelectric properties of materials with chemical bond hierarchy will be further explored.

### Broader impact (Optional for DOE grants/FWPs)

Our project has been supporting 3 graduate students and one postdoc. One graduate student recently successfully defended his Ph. D. thesis. All of them had interaction with our industrial partners at GM R&D center in terms of materials synthesis, measurement, and data analysis.

### Data Management and Open Access

The data and computational codes developed have been published and are available for public.

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# Engineering Organic Glasses

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**Keywords:** Glass, anisotropic packing, molecular orientation, kinetic stability, crystallization

## Project Scope

Glasses are remarkable materials with liquid-like spatial uniformity and crystal-like strength, making them useful for many applications. Traditional liquid-cooled glasses often suffer the shortcomings of structural relaxation and shrinkage over time. Furthermore, they are usually isotropic. By physical vapor deposition (PVD), the team aims to produce high-density, high-stability glasses with active control over molecular orientation. Concurrent simulations study the mechanism by which these remarkable materials are produced. Polymer additives are used to stabilize organic glasses against crystallization. The highly stable glasses with controlled molecular packing are potentially useful for drug delivery, bio-preservation, and organic electronics. They expand the range of materials available for designing new products with advanced applications.

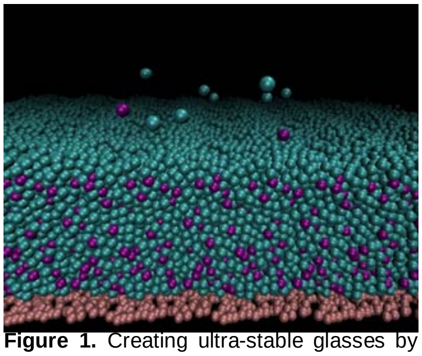

**Figure 1.** Creating ultra-stable glasses by computer simulations, in which vapor molecules are gradually deposited into the free interface of a growing film.

**Relevance to MGI.** There have been strong interactions between theory and experiment, as documented below

## Technical Progress

**Stable Glasses by PVD with Control over Molecular Orientation.** Recent experiments indicate that PVD glasses can be much more stable than traditional liquid-cooled glasses and might correspond to equilibrium states that could hitherto be reached only by glasses aged for thousands of years. We created ultrastable glasses by computer simulation that mimics PVD. These stable glasses have the properties expected for the equilibrium supercooled liquid state, and optimal stability is attained on deposition at the Kauzmann temperature (Papers 1&2). Applying the methodology to the PVD glasses of short polymer chains (3), we found the resulting glasses are denser and kinetically more stable than liquid-cooled glasses. Glasses deposited slowly at the optimal substrate temperature correspond to ordinary glasses prepared by cooling the liquid at rates 4–5 orders of magnitude slower than those accessible in the current simulations. For intermediate length polymer chains, PVD glasses are highly anisotropic. For short chains, however, they are isotropic, showing that structural anisotropy is not a necessary condition for formation of stable glasses by PVD.

A fruitful interaction between experiment and theory revealed the mechanism by which PVD creates glasses that have preferred and tunable molecular orientations (4). We apply a high-throughput scheme to investigate the effect of the substrate temperature ($T_{Substrate}$) on glasses of organic semiconductors. We find that molecular orientation in these glasses is continuously tunable and controlled by $T_{Substrate}/T_g$,

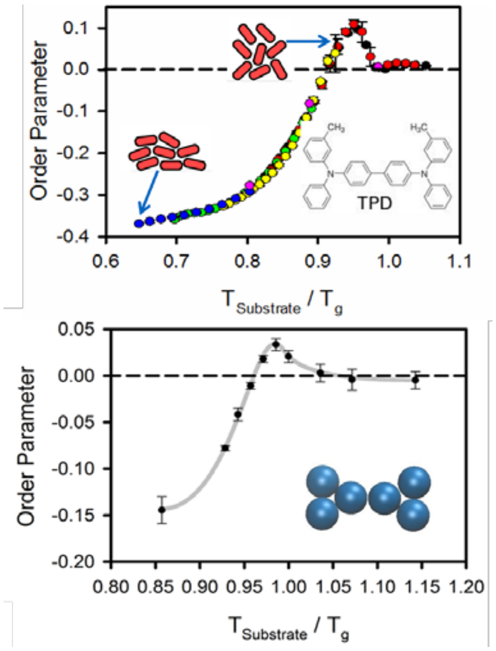

**Figure 2.** Molecular orientation in PVD glasses can be controlled by the substrate temperature (upper panel). Molecular orientation can increase the efficiency of organic electronics such as OLEDs. Computer simulations reproduce the experimental trends and explain the result in terms of preferred orientation at the surface of the equilibrium liquid and the ability to reach local equilibrium at a given substrate temperature (lower panel).

where $T_g$ is the glass transition temperature. All molecules tested can produce highly anisotropic glasses, with similar dependence of molecular orientation on substrate temperature. Simulations reproduce the experimental trends and explain molecular orientation in the deposited glasses in terms of surface properties of the equilibrium liquid. These results provide an avenue for performance optimization of active layers in organic electronics.

**Understanding and Controlling Crystallization in Molecular Glasses.** Fast crystal growth abruptly can emerge as molecular liquids are cooled to become glasses. This Glass-to-Crystal (GC) mode can cause crystallization rates $10^4$ times faster than predicted by standard models and threaten the stability of amorphous materials. We studied this phenomenon in 12 systems (5), including two that are structurally homologous and dynamically similar to the model glassformer *ortho*-terphenyl (OTP) (6). While the 12 systems differ greatly with growth rates spanning $10^4$ times, the general condition for GC growth is that liquid diffusion be slow relative to crystal growth according to $D/u$ < 7 pm. This condition suggests that the phenomenon is a solid-state process terminated by fluidity. GC growth must solidify several molecular layers before rearrangement by diffusion.

We studied crystal growth in organic glasses in the presence of low-concentration polymers to discover design principles for crystallization inhibitors (7). Doping the organic glass nifedipine (NIF) with 1 wt % polymer has no effect on the $T_g$ of host molecules, but substantially alters the rate of crystal growth. The crystal growth rate varies exponentially with polymer concentration, in analogy with the polymer effect on solvent mobility. The ability to inhibit crystal growth is not ordered by the strength of host-polymer hydrogen bonds, but correlates with the polymer's $T_g$, suggesting that the mobility of polymer chains controls their inhibition of crystal growth.

**Future Plans**. (1) PVD of molecules with liquid-crystalline order. Preliminary indications are that these materials are more anisotropic than previously deposited PVD glasses. (2) PVD of azobenzenes in the presence of optical fields to control molecular conformation in molecular glasses. (3) Determine the factors that define effective inhibitors of crystallization with focus on segmental mobility and hydrogen bonding.

**Broader impact.** The project has involved 11 graduate students, 3 postdocs, and 3 undergraduates. They worked in a highly interdisciplinary environment. Some have graduated to become independent researchers and educators. Personnel supported by this grant worked with UW-Madison's Pre-college Enrichment Opportunity Program for Learning Excellence (PEOPLE), which has a proven record of increasing the enrollment of minority and low-income high school students to colleges and universities. This program provides experiences that help students to become scientifically literate citizens and encourages them to consider careers in science and engineering.

**Data Management and Open Access.** Our data were published in widely accessible journals.

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# Design Knowledge Base of Low-Modulus Titanium Alloys for Biomedical Applications

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**Keywords:** Ti-Mo-Nb-Ta-Zr, Elasticity, Diffusivity, Thermodynamics, Biomedical

## Project Scope

This project aims to establish a fundamental knowledge base to enable accelerated design of advanced Ti alloys for biomedical prosthetic devices, i.e., alloys with elastic modulus matching that of bone (20-30 GPa). To this vision, an effective approach in terms of high-throughput computational predictions and high-throughput experimental validations will be employed to establish CALPHAD-type digital databases of elasticity, diffusivity, and thermodynamics in the Ti-Mo-Nb-Ta-Zr system. In turn, new alloying and processing concepts will be brought forward to design low-modulus Ti alloys for biomedical applications.

## Relevance to MGI

To achieve the project scope, an integrated approach is being used, including (i) high-throughput computational tools of first-principles calculations and CALPHAD modeling, (ii) high-throughput experimental tools using such as diffusion multiple and Laser Engineered Net Shaping (LENS) processed gradient composition samples, and (iii) the to be established digital data of elasticity, thermodynamics, and diffusivity for the Ti-Mo-Nb-Ta-Zr system. As an example, first-principles predicted dilute diffusion coefficients of alloying elements X in hcp Ti are show in Figure 1.

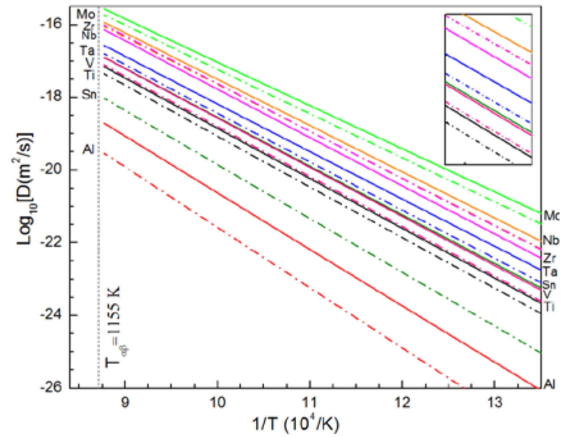

**Figure 1.** First-principles predicted dilute diffusion coefficients D for alloying elements X in hcp Ti. Dashed lines // c-axis, and solid lines ⊥ c-axis.

## Technical Progress

This project was started in Fall 2013, and current technical progress includes the following four aspects:

1. *Diffusion coefficients of alloying elements in the Ti-Mo-Nb-Ta-Zr system*: In terms of computational simulations, we predicted the dilute diffusivity coefficients of seven alloying elements in hcp Ti by using the eight-frequency model and first-principles calculations [1], the results are detailed in Figure 1. In terms of high-throughput experimental measurements, diffusion multiples have been designed for the Ti-Mo-Nb, Ti-Mo-Ta, Ti-Mo-Zr, Ti-Nb-Ta, and Ti-Ta-Zr alloys, and these experiments are ongoing.
2. *Elastic properties for alloys in the Ti-Mo-Nb-Ta-Zr system*: In terms of computational simulations, we are predicting mainly elastic properties for the bcc-based Ti-X and Ti-X-Y alloys (X and Y are alloying elements) by using an efficient first-principles strain-stress method [2]. As an example, Figure 2 shows a comparison of Young's modulus for the Ti-Ta alloys from both experiment and first-principles calculations. In terms of high-throughput experiments, the localized elastic constants will be measured from diffusion multiple samples and the LENS processed gradient composition samples, and these experiments are ongoing.
3. *Thermodynamic (CALPHAD) modeling of the Ti-Mo-Nb-Ta-Zr system*: In terms of computational simulations, CALPHAD modeling approach [3] using data from first-principles calculations and experiments in the literature or from the present work (see below) will be used to model the binary Ti-X and ternary Ti-X-Y systems. Specially, we are modeling the Ti-Sn binary system and the Ti-Ta-Na and Ti-Ta-Mo ternary systems. In terms of high-throughput experiments, phase relations from diffusion multiples will be used to validate the modeled phase diagrams, and currently these works are ongoing.

## Future Plans

In the future, we will continue to do the work related to elasticity, diffusivity, and thermodynamics in the Ti-Mo-Nb-Ta-Zr system. Special tasks are listed in the following for these three aspects:

1. *Diffusion coefficients of alloying elements*: Dilute diffusion coefficients of alloying elements in hcp Ti; Test of methodology: diffusion coefficients in concentrated Ti alloys with bcc structure
2. *Elastic properties*: Ti-Ta system: elasticity of bcc and hcp phases from both first-principles calculations and combinatorial experiments; Ti-X (X = Mo, Nb, Ta, Zr) systems: elasticity of bcc based alloys from first-principles calculations and experiments
3. *Thermodynamic (CALPHAD) modeling*: Ti-Sn system: this work will be completed; A preliminary thermodynamic database of the Ti-Mo-Nb-Ta-Zr system will be built

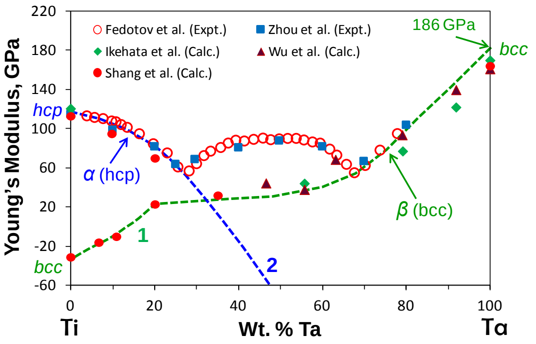

**Figure 2.** Comparison Young's modulus of the Ti-Ta alloys from experiments (room temperature) and first-principles calculations (0 K results). The present work indicated by Shang *et al.*, and the lines guide for eye.

## Broader impact

Biocompatible Ti alloys with low elastic modulus are considered to be one of the best options for prosthetic implants. The ability to tailor the composition and microstructure to design alloys to meet specific property requirements is the goal of MGI in general and the purpose of this study in particular. The biocompatible, low modulus Ti alloys are a perfect test bed for MGI since on the one hand their complexity requires the use of all the tool sets of MGI, but on the other hand they are sufficiently "simple" for the tools to make a real difference in alloy development. The timely design and insertion of high-performance materials are critical to the global competitiveness of US manufacturing as well as minimization of the negative impact to the environment. This NSF program is educating next-generation materials scientists and engineers who will master both advanced computational and experimental approaches with cross-disciplinary knowledge of materials to better serve society. The research and education of the proposed study will also help usher in a new paradigm of materials research and innovation where materials design is conducted by up-front simulations followed by key validation experiments in contrast to the current approach that is heavily based on experimental iterations followed by mechanistic characterization/explanations.

## Data Management and Open Access

Data and samples to be generated in the research section of this project will be placed into two categories – physical samples and records of sample and simulation characteristics. Physical samples will consist of titanium alloys for biomedical applications at all stages in design and test. Records will include digital files of simulation, characterization, and performance results, along with both digital and hand-written lab notebook records of procedures and practices used. Calculations using Density Functional Theory will be performed to gain insight into elastic, thermodynamic and diffusion properties of stable and unstable phases. Output will be electronic files and plots. The data sets are generally in binary or ASCII format readable by common data analysis and/or graphical analysis programs (e.g., Microsoft Excel, SigmaPlot, Origin). The PI's and co-PI's laboratories are open to sharing results in any form with interested parties upon request. The results of the work are archived in peer-reviewed publications, that will include much of the primary data resulting from the work, e.g. plots of XRD patterns, tables of data (e.g., crystallographic data, peak positions) or images (e.g., SEM micrographs, TEM cross-sections). A second product of the research project is theses or dissertations authored by graduates who conduct the work. Typically the dissertations will contain much of the primary results of the work.

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## Publications

The following two manuscripts were partially supported by this award.

1. Z. K. Liu, Y. Wang, and S. L. Shang, *Thermal expansion anomaly regulated by entropy*, Sci. Rep. **4**, 7043 (2014).
2. F. L. Dri, S. L. Shang, L. G. Hector Jr., P. Saxe, Z. K. Liu, R. J. Moon, P. D. Zavattieri, "*Anisotropy and temperature dependence of structural, thermodynamic, and elastic properties of crystalline cellulose* $I_\beta$*: A first-principles investigation*", Modelling Simul. Mater. Sci. Eng. **22**, 085012 (2014).

# Theory-guided experimental search of new classes of designed topological insulators

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**Co-Principle Investigators** Dan Dessau CU Boulder dan.dessau@colorado.edu, Gang Cao University of Kentucky cao@pa.uky.edu.
**Investigators:** Qihang Liu, Xiuwen Zhang, Justin Waugh, Xiaoqing Zhou, and CU Boulder.
**Keywords:** Topological insulators, Spin-polarization; ARPES; DFT; 'Inverse Design'.

**Project Scope:** We accelerate material development by using *Functionality-Directed material discovery* (also called 'Inverse Design') as follows (a) Develop a science-based "Design Principle" (DP) that reflects a target functionality (F) we are searching for (E.g., for F = topological insulation, DP = specific band inversions). (b) Search via DFT for the specific DP in groups of materials in assumes structures (c) Select those that best satisfy the DP and are thermodynamically stable according to DFT. (d) After narrowing down large pools of potential candidates, subject the "best of class" cases to synthesis and characterization of F. Iterations and feedback are used to refine the DP. In the current DMREF we focus on F = Topological insulation and F = Hidden spin polarization described under Technical Progress.
**Relevance to MGI:** This project uses theory-directed screening of materials based on Design Principles. Acceleration emerges from dual screening for functionality and growability. We close the loop by iterative feedback between synthesis and properties measurement and theory. **Technical Progress:**
***(1) Associating specific stable materials with Topological Insulation and other band-inverted behaviors*:** We identify two generic prototypes of topological insulators TI-1 and TI-2 and two band-inverted insulators BI-3 and BI-4 based on the number of bands that switch positions at the time reversal invariant momenta (TRIM) representing a given valley in the Brillouin zone. We then search via DFT if the crystal structure S carrying this functionality S(BI-i) and S(TI-i has the additional virtue of being thermodynamically stable, and if not, how metastable is it. A number of TI and BI materials are being discovered. "Best of class" candidates are passed on to our experimental team for synthesis and spin-ARPES. We find that many (but not all) materials identified as Topological Insulators on the basis of calculation of band inversion are thermodynamically unstable in the structure S that makes them TI's. In turn, the thermodynamically stable structure is often not a TI. Examples include $SrTeO_3$, $BaTeO_3$that are TI-1 in the presumed cubic perovskite (Pm-3m) structure, which is thermodynamically unstable; their ground state structures (space groups P1, $P2_1/m$) are not TI-1. Similarly, a special form of "Band Inversion 4" (defined by having a total *even* number of band inversions at TRIMs that each has even-fold valley degeneracy) has been suggested for $Sr_3PbO$ and $Sr_3SnO$ in assumed cubic anti-perovskite structures that we find, however to be highly unstable to decomposition. ***Emerging* Conjecture:** Multiple band inversions -- associated with occupation of *anti bonding* conduction bands and emptying of bonding valence bands—may be contraindicated with thermodynamic stability. ***(2) Discovering 'Hidden Spin Polarization' in centrosymetric crystals:*** We have proposed **[1, 2]** a novel form of "hidden spin Polarization" that would be present in materials that have strong SOC but are centrosymmetric, so by common understanding should *not* have Rashba (R-1) or Dresselhause (D-1) spin polarization. We show that they do have another form of spin polarization (called R-2 and D-2). Examples include $LaBiOS_2$ being grown and examined by spin-ARPES by our team. We searched the group of $M'OMX_2$ [2] and found more R-2 and D-2 materials. ***(3) Prediction of circular polarization in even-monolayer centrosymmetric transition-metal dichalcogenides [3]***: The circular polarization (CP) that the photoluminescence inherits from the excitation source in n monolayers of transition-metal dichalcogenides $(MX_2)_n$ has been previously explained as a special feature of *odd* values of n, where the inversion symmetry is absent. We show that also for n = even where inversion symmetry is present and

valley polarization physics is strictly absent, intrinsic selectivity in CP is to be expected on the basis of fundamental spin-orbit physics discussed in item (2) above. First-principles calculations of CP predict significant polarization for n = 2 bilayers: from 69% in $MoS_2$ to 93% in $WS_2$. This discovery broadens the range of materials to be considered as CP sources. ***(4) Switching a normal insulator to a topological insulator by electric field [4]:*** Using first-principles calculations with applied perpendicular electric field $F_\perp$ we predict a transition from the normal insulator to a topological insulator and eventually to a metal as a function of $F_\perp$. This is applied to Phosphorene, a two-dimensional (2D) material that can be isolated through mechanical exfoliation from layered black phosphorus. The tuning of topological behavior with electric field would lead to spin-separated, gapless edge states, i.e., quantum spins Hall effect. Insights drawn are used to formulate design principles for looking for other 2D materials that could have such an electrical-induced topological transition. This sets the stage for broadening the TI materials base by F field. **Future Plans:** center on accelerated experimental validation of theoretical predictions, including (i) the 'hidden spin polarization' predicted in $LaOBiS_2$ will be tested via spin-ARPES. Targeted surface calculations will be performed to compare with measured spin polarization in spin-ARPES experiments. (ii) A number of never before made materials predicted to be TI-1 and TI-2 will be made and examined experimentally. (iii) Additional collaborations are formed with experimental groups interested to examine our prediction of CP in MX2 (item (3) and field-induced TI-ness in black Phosphorus (item 4). **Broader impact:** (i) This project will validate ***a general platform for discovery of functional materials,*** as described under "scope". Although we focus here on SOC enabled functionalities, the ideas behind this "inverse Design" have far broader implications for discovery many other technology-enabling materials with specialized functionalities. These are otherwise difficult to detect via trial and error or serendipity and include such as 'oxides for electronics' or 'super absorbers for renewable energy ' or thermoelectrics. (ii) The specific subject matter dealt with in this DMREF is instrumental for training next generation workforce in materials research and for the education of students. (iii) The specific discoveries of novel physics (such as hidden spin polarization; the possible dichotomy between multiple band inversions and thermodynamic stability) has strong intellectual weight as noted by the Nature editorial in Ref 1 stating that this will require text books to be re written. **Data Management and Open Access (i)** The codes that analyze the first principles wave functions to obtain information of band inversions and topological invariant $Z_2$, will be opened for public access. (ii) The materials predicted in this study will be made publically accessible. (iii) The theoretical data is currently saved in Extreme Science and Engineering Discovery Environment (XSEDE), which will be transferred to publically accessible sources. **Publications credited to DMREF**

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# *Poster List*

# DOE/NSF Materials Genome Initiative Principal Investigators' Meeting

## Poster Session I

## Monday, January 12, 2015

1. **Nicholas L. Abbott**, University of Wisconsin-Madison
   *Collaborative Research: Chemoresponsive Liquid Crystals Based on Metal Ion-Ligand Coordination*

2. **Sean R. Agnew**, University of Virginia
   *Multi-Scale Modeling and Characterization of Twinning-Induced Plasticity and Fracture in Magnesium Alloys*

3. **John Allison**, University of Michigan
   *Center for PRedictive Integrated Structural Materials Science (PRISMS)*

4. **Alan Aspuru-Guzik**, Harvard University
   *Towards 3rd Generation Organic Tandem Solar Cells with 20% Efficiency: Accelerated Discovery and Rational Design of Carbon-Based Photovoltaic Materials Through Massive Distributed Volunteer Computing*

5. **David Baker**, University of Washington
   *Integrating Theory, Computation and Experiment to Robustly Design Complex Protein-Based Nanomaterials*

6. **Zhenan Bao**, Stanford University
   *Predict Blend Morphology of Organic Photovoltaic Materials*

7. **Mark Bathe**, Massachusetts Institute of Technology
   *Computational Design Principles for Functional DNA-based Materials*

8. **Rajendra K. Bordia**, Clemson University
   *Multi-Scale Fundamental Investigation of Sintering Anisotropy*

9. **Michael P. Brenner**, Harvard University
   *Control of Colloidal Assemblies Using Dynamic DNA Nanostructures*

10. **R. Morris Bullock**, Pacific Northwest National Laboratory
    *Molecular Electrocatalysis for Hydrogen Production: Make, Measure and Model at its Best*

11. **William H. Butler**, University of Alabama
    *First-Principles Based Design of Spintronic Materials and Devices*

12. **Marie-Carme Calderer**, University of Minnesota
    *Materials Engineering of Chromonic and Colloidal Liquid Crystals via Mathematical Modeling and Simulation*

13. **R. W. Carpick**, University of Pennsylvania
    *High-Throughput Discovery, Development and Demonstration of Material Systems to Enable Low-Power NEMS-Based Computation*

14. **Michael Chabinyc**, University of California Santa Barbara
    *Controlling Hierarchical Nanostructures in Conjugated Polymers*

15. **K. S. Ravi Chandran**, University of Utah
*Computational Design, Rapid Processing and Characterization of Multiclass Materials from Genomic Ti-B-X Platform*

16. **James R. Chelikowsky**, University of Texas at Austin
*Collaborative Research for the Design and Synthesis of Novel Magnetic Materials*

17. **Peter C. Collins**, University of North Texas
*Collaboration to Accelerate the Discovery of New Alloys for Additive Manufacturing*

18. **Michael J. Demkowicz**, Massachusetts Institute of Technology
*Inferring Grain Boundary Properties from Heterogeneous Data*

19. **Chang-Beom Eom**, University of Wisconsin-Madison
*Multifunctional Interfacial Materials by Design*

20. **Elif Ertekin**, University of Illinois
*Discovery and Design of Ferromagnetic Shape Memory Alloys by Quantum Mechanical Simulation and Experiment*

21. **Horacio D. Espinosa**, Northwestern University
*Advanced Material Based on Atomically Thin Layered Building Blocks—Iterative Design Based on Chemistry and Topology*

22. **Glenn H. Fredrickson**, University of California, Santa Barbara
*Computationally Driven Discovery and Engineering of Multiblock Polymer Nanostructures Using Genetic Algorithms.*

23. **C. M. Friend**, Harvard University
*Integrated Mesoscale Architectures for Sustainable Catalysis*

24. **Filipp Furche**, University of California, Irvine
*Non-Adiabatic Molecular Dynamics Methods for Materials Discovery*

25. **Laura Gagliardi**, University of Minnesota
*Inorganometallic Catalyst Design Center Energy Frontier Research Center*

26. **Daniel Gall**, Rensselaer Polytechnic Institute
*Nitride Discovery Creating the Knowledge Base for Hard Coating Design*

27. **William A. Goddard III**, California Institute of Technology
*Multiscale Theory and Experiment in Search for and Synthesis of Novel Nanostructured Phases in BCN Systems*

28. **Jeffrey Greeley**, Purdue University
*Design of Multifunctional Catalytic Interfaces from First Principles*

29. **Francois Gygi**, University of California Davis
*High-Performance First-Principles Molecular Dynamics for Predictive Theory and Modeling*

30. **Ronald C. Hedden**, Texas Tech University
*Combinatorial Methods to Enable Rapid Prototyping of Polymeric Pervaporation Membranes for Biofuels*

31. **Hendrik Heinz**, University of Akron, Ohio
*Design and Testing of Nanoalloy Catalysts in 3D Atomic Resolution*

32. **John M. Herbert**, The Ohio State University
    *Efficient Methods for Computing High-Accuracy Non-Covalent Interaction Energies in Clusters, Liquids, and Molecular Crystals*

33. **Elizabeth A. Holm**, Carnegie Melon University
    *Mechanics of Three-Dimensional Carbon Nanotube Aerogels with Tunable Junctions*

34. **Kendall N. Houk**, University of California Los Angeles
    *Iterative Theoretical Morphology Prediction, Synthesis, and Characterization of Novel Donor Oligomers for Accelerated Materials Discovery*

35. **Robert Hull,** Rensselaer Polytechnic Institute
    *Real Time Control of Grain Growth in Metals*

36. **Michael J. Janik**, Pennsylvania State University
    *Computationally Guided Design of Multicomponent Materials for Electrocatalytic Reactions*

37. **Jeremiah A. Johnson**, Massachusetts Institute of Technology
    *Analysis and Optimization of Polymer Networks for Emerging Applications*

38. ***Peter Johnson**, Brookhaven National Laboratory*
    *Center for Emergent Superconductivity*

39. **Yung Joon Jung,** Northeastern University
    *Engineering Strong, Highly Conductive Nanotube Fibers via Fusion*

40. **Paul R. C. Kent,** Oak Ridge National Laboratory
    *Network for Ab Initio Many-Body Methods: Development, Education and Training*

41. **Sinan Keten,** Northwestern University
    *Simulation-Based Design of Functional Sub-nanometer Porous Membranes*

42. **Thomas Keyes,** Boston University
    *Combining Novel Simulation Methods and Nucleation Theory to Uncover the Secrets of Gas Hydrates*

43. **John Kieffer**, University of Michigan
    *Simulation-Based Predictive Design of All-Organic Phosphorescent Light-Emitting Molecular Materials*

44. **Sanat Kumar,** Columbia University
    *DNA-Grafted Building Blocks Designed to Self-Assemble into Desired Nanostructures*

45. **Shyue Ping Ong**, University of California San Diego
    *Design of Novel Sodium Superionic Conductors using Integrated High-throughput First Principles Calculations, Data Mining and Experiments*

46. **Thomas Proffen,** Oak Ridge National Laboratory
    *Center for Accelerating Materials Modeling (CAMM) from SNS Data*

47. **Sergei S. Sheiko**, University of North Carolina at Chapel Hill
    *Acoustically Transformative Materials*

48. ***Samuel Stupp**, Northwestern University*
    *EFRC Center for Bio-Inspired Energy Science*

# DOE/NSF Materials Genome Initiative

# Principal Investigators' Meeting

## Poster Session II

## Tuesday, January 13, 2015

1. **Stephen J. Klippenstein**, Argonne National Laboratory
   *An Expert Ab Initio Transition-State-Theory-Based Master Equation Code*

2. **Irena Knezevic,** University of Wisconsin-Madison
   *Coupling Electrons, Phonons, and Photons for Nonequilibrium Transport Simulation*

3. **Robert V. Kohn**, New York University
   *Adaptive fine-scale structure design: from theory to fabrication*

4. **Enrique Lavernia**, University of California, Davis
   *Engineering Strength and Toughness into Metals*

5. **James P. Lewis**, West Virginia University
   *Designing Tunable Au-Based Bimetallic Nanocatalysts*

6. **Peter Littlewood**, Argonne National Laboratory
   *Machine Learning for Many-Body Physics*

7. **Jeffrey Long,** University of California, Berkeley
   *Center for Gas Separations Relevant to Clean Energy Technologies*

8. **Neepa T. Maitra,** Hunter College
   *Electron-Ion Dynamics with Time-Dependent Density Functional Theory: Towards Predictive Solar Cell Modeling*

9. **Patrick T. Mather**, Syracuse University
   *Laminated Elastomeric Composites with Anisotropic Shape Memory*

10. **Paul McEuen,** Cornell University
    *Graphene based Origami and Kirigami Metamaterials*

11. **Efstathios I. Meletis**, University of Texas at Arlington
    *Multiscale Design of Hard and High Temperature Resistant Coatings by Computation and Experiment.*

12. **Thomas Miller**, California Institute of Technology
    *Next-generation Nanostructured Polymer Electrolytes by Molecular Design*

13. **Tim Mueller**, Johns Hopkins University
    *Design of Nanoscale Alloy Catalysts from First Principles*

14. **Jens K. Nørskov**, SLAC National Accelerator Laboratory, Stanford University
    *Predictive Theory of Transition Metal Oxide Catalysis*

15. **John B. Parise,** Stony Brook University and Brookhaven National Laboratory
    *High-Pressure Synthesis Directed by Theory*

16. **John P. Perdew,** Temple University
    *New Energy Frontier Research Center: Center for the Computational Design of Functional Layered Materials (CCDM)*

17. **John H. Perepezko,** University of Wisconsin-Madison
    *A Combined Experiment and Simulation Approach to the Design of New Bulk Metallic Glasses*

18. **Kristin A. Persson**, Lawrence Berkeley National Laboratory
    *The Materials Project: Merging Ab Initio Calculations, Supercomputing, and Data Science for Materials Genomics*

19. **Darrin Pochan,** University of Delaware
    *Programmable peptide-based hybrid materials*

20. **Tresa Pollock,** University of California Santa Barbara
    *Discovery, Development and Deployment of High Temperature Coating – Substrate Systems*

21. **Karin M. Rabe**, Rutgers University
    *High-Throughput Mapping of Functional Dielectric-Metallic Heterostructures*

22. **Aldo Humberto Romero**, West Virginia University
    *Search for Magneto-electronic Behavior in Complex Fluoride-based Interfaces*

23. **Gregory C. Rutledge,** Massachusetts Institute of Technology
    *Discovery and Development of Additives for Novel Polymer Morphology and Performance*

24. **Jan Schroers**, Yale
    *High-Throughput Simulations and Experiments to Develop Metallic Glasses*

25. **J. Ilja Siepmann,** University of Minnesota
    *Nanoporous Materials Genome: Methods and Software to Optimize Gas Storage, Separation, and Catalysis*

26. **Randall Q. Snurr**, Northwestern University
    *Simulation-Driven Design of Highly Efficient MOF/Nanoparticle Hybrid Catalyst Materials*

27. **Volker Sorger**, The George Washington University
    *Theory-enabled Development of 2D Metal Dichalcogenides as Active Elements of On-chip Silicon-Integrated Optical Communication*

28. **Eric Toberer,** Colorado School of Mines
    *Computationally Driven Targeting of Advanced Thermoelectric Materials*

29. **William Tumas,** National Renewable Energy Laboratory
    *Center for Next Generation of Materials by Design (CNGMD) Energy Frontier Research Center*

30. **Yasutomo Uemura**, Columbia University
    *Designing, Understanding and Functionalizing Novel Superconductors and Magnetic Derivatives*

31. **Chris G. Van de Walle**, University of California, Santa Barbara
    *Design and Fabrication of Wide-Band-Gap Nitride-Based Alloys*

32. **Anton Van der Ven**, University of California Santa Barbara
    *Integrated Computational Framework for Designing Dynamically Controlled Alloy-Oxide Heterostructures*

33. **David Vanderbilt,** Rutgers University
    *Enhanced Functionalities in 5d Transition-Metal Compounds from Large Spin-orbit Coupling*

34. **Dionisios (Dion) G. Vlachos,** University of Delaware
*In Silico Prediction of Catalytic Materials for Biomass Upgrade in the Catalysis Center for Energy Innovation*

35. **Krista Walton,** Georgia Institute of Technology
*Materials Modeling in the Center for Understanding and Control of Acid Gas-Induced Evolution of Materials for Energy (UNCAGE-ME)*

36. **Yunzhi Wang**, The Ohio State University
*Accelerated Development of Next Generation Ti Alloys by ICMSE Exploitation of Non-Conventional Transformation Pathways*

37. **Michael Weinert**, University of Wisconsin-Milwaukee
*Emergent Functionalities at the Epitaxial Interfaces of Correlated and Spin-Orbit Materials*

38. **Steven R. White**, University of California
*Strong Correlation, DMRG and DFT*

39. **Jihui Yang**, University of Washington
*High Efficiency Hierarchical Thermoelectric Composites by Multiscale Materials Design and Development*

40. **Lian Yu**, University of Wisconsin – Madison
*Engineering Organic Glasses*

41. **Ji-Cheng Zhao**, The Ohio State University
*Design Knowledge Base of Low-Modulus Titanium Alloys for Biomedical Applications*

42. **Alex Zunger**, Colorado University
*Theory-guided Experimental Search of New Classes of Designed Topological Insulators*

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