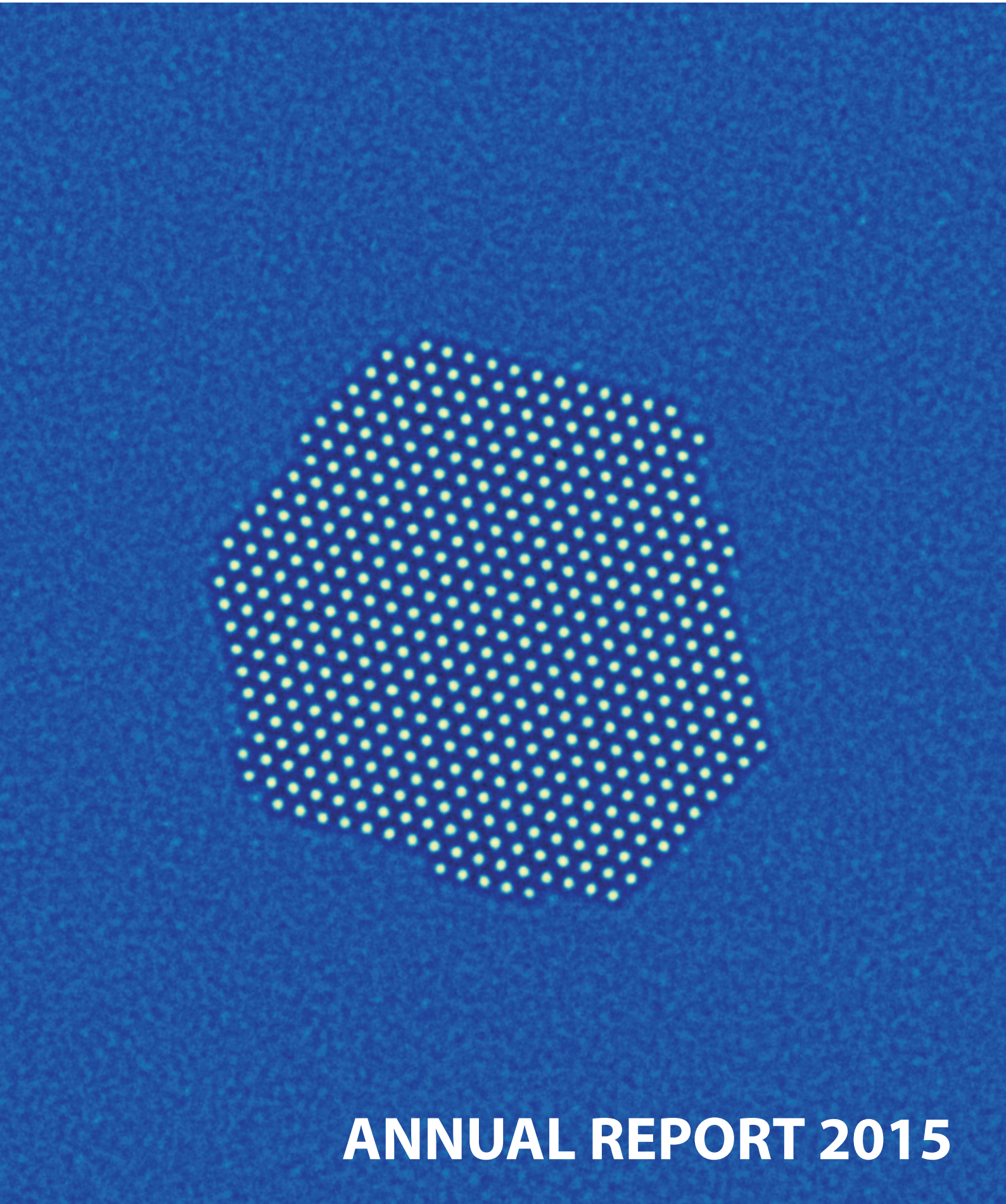
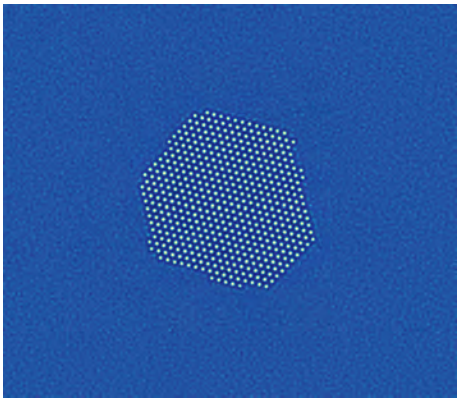
CHiMaD

Center for Hierarchical Materials Design



ANNUAL REPORT 2015

On the cover: Simulation of out of equilibrium solidification of a faceted crystal in the presence of thermal fluctuations. The atomic probability density of the crystal lattice is shown. Clearly shown is the ledge nucleation and growth mechanism, a hallmark of faceted systems. See Chapter 16 (Nana Ofori-Opoku, NIST-CHiMaD Postdoctoral Research Fellow)



Editor:
Emine Begum Gulsoy, Ph.D.
CHiMaD Associate Director

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CHiMaD 2015

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Center for Hierarchical Materials Design

1. Center for Hierarchical Materials Design

Foreword

We are pleased to present the second annual report of the Center for Hierarchical Materials Design (CHiMaD), the National Institute for Standards and Technology (NIST) Center of Excellence in Advanced Materials. CHiMaD has become a focal point, both nationally and internationally, for the Materials Genome Initiative (MGI). We are committed to achieving the goals of the MGI through the development of broad research and outreach programs that involve participants from universities, national laboratories and companies. Bringing together researchers with expertise in computation, data science, and experiment to focus on the design of new materials is at the core of both the MGI and the CHiMaD. These collaborative efforts show the power of incorporating experimental and computational databases in the materials design process.

Along with scientists and engineers from the National Institute for Standards and Technology, we are demonstrating the power and potential of the MGI by designing novel materials ranging from cobalt alloys to polymers for photovoltaics. The design effort compasses 36 principal investigators, 34 postdoctoral research fellows, 38 graduate students and 7 undergraduate students working in the CHiMaD use-case groups along with 3 technical staff members and 40 NIST collaborators. This report presents the objectives and accomplishments of our use-case groups, seed groups, and multiple tool development efforts. The breadth of our portfolio allows us to interact with a diverse array of industrial partners. We are also a resource for the Nation through the sponsorship of workshops, on topics such as community standard codes for phase field methods, materials design, mutivalent interactions in polyelectrolytes, and industrial alloy design and development, as well as by providing tools and databases, such as the Materials Data Facility (MDF), for the community. The MDF will serve as a resource for sharing, storing, and mining the large datasets that are being produced by state-of-the-art experimental facilities. Even though we are only in our second year, CHiMaD's research portfolio has evolved with the expansion of efforts in additive manufacturing and a reduction of our work on Si-based structural alloys.

With our increasing national and international visibility and many design efforts that are moving forward with great speed, we are making the promise of the Materials Genome Initiative a reality. We look forward to another exciting year.

Peter Voorhees, Juan de Pablo, Gregory Olson
CHiMaD Co-Directors

Mission and Vision

Accelerating materials discovery and commercialization by design and development of hierarchical methods and materials and enabling the complete integration of computation, experimentation and databases by building a strong community of current and future researchers

Center for Hierarchical Materials Design (CHiMaD) is a NIST-sponsored center of excellence for advanced materials research that is focused on developing the next generation of computational tools, databases and experimental techniques in order to enable the accelerated design of novel materials and their integration to industry, one of the primary goals of the *Materials Genome Initiative (MGI)*.

This Chicago-based consortium includes Northwestern University (NU) as the lead, University of Chicago (UChicago), Northwestern-Argonne Institute for Science and Engineering (NAISE), a partnership between Northwestern University and Argonne National Laboratory (ANL), and the Computational Institute (CI), a partnership between University of Chicago and Argonne National Laboratory. The consortium is also partnered with Questek Innovations (QT), a pioneering materials design company, ASM International and Fayetteville State University.

Designing novel materials of specific properties for a particular application requires simultaneously utilizing physical theory, advanced computational methods and models, materials properties databases and complex calculations. This approach stands in contrast to the traditional trial-and-error method of materials discovery. CHiMaD aims to focus this approach on the creation of novel *hierarchical materials* which exploit distinct structural details at various scales, from the atomic on up, to obtain enhanced properties. The center's research focuses on both organic and inorganic advanced materials in fields as diverse as self-assembled biomaterials, smart materials for self-assembled circuit designs, organic photovoltaic materials, advanced ceramics and metal alloys.

Objectives

- To *foster* hierarchical materials discovery, in accordance with the goals of MGI and NIST, by developing the next generation of computational tools, databases and experimental techniques.
- To *connect* and *convene* the current experts and the next generation of scientists by advancing the multi-disciplinary and multi- sector communication through workshops, seminars, training opportunities and meetings
- To *provide* opportunities to transition new breakthroughs in advanced materials to industry
- To *adopt* a seamless integration of prediction, measurement and interpretation
- To *maintain* and *advance* the collective knowledge on material systems and methodologies and to *serve*, together with NIST, as a national resource for verified codes and curated databases that will enable proliferation of a materials-by-design strategy and materials discovery through US industry partners
- To *build* on the established success in metal alloy systems to prove generality of the materials- by-design approach through application to both inorganic and organic advanced systems for both structural and multifunctional applications
- To *expand* the 3D and 4D characterization methods for hard materials design and to bring such methods to the forefront of soft materials design

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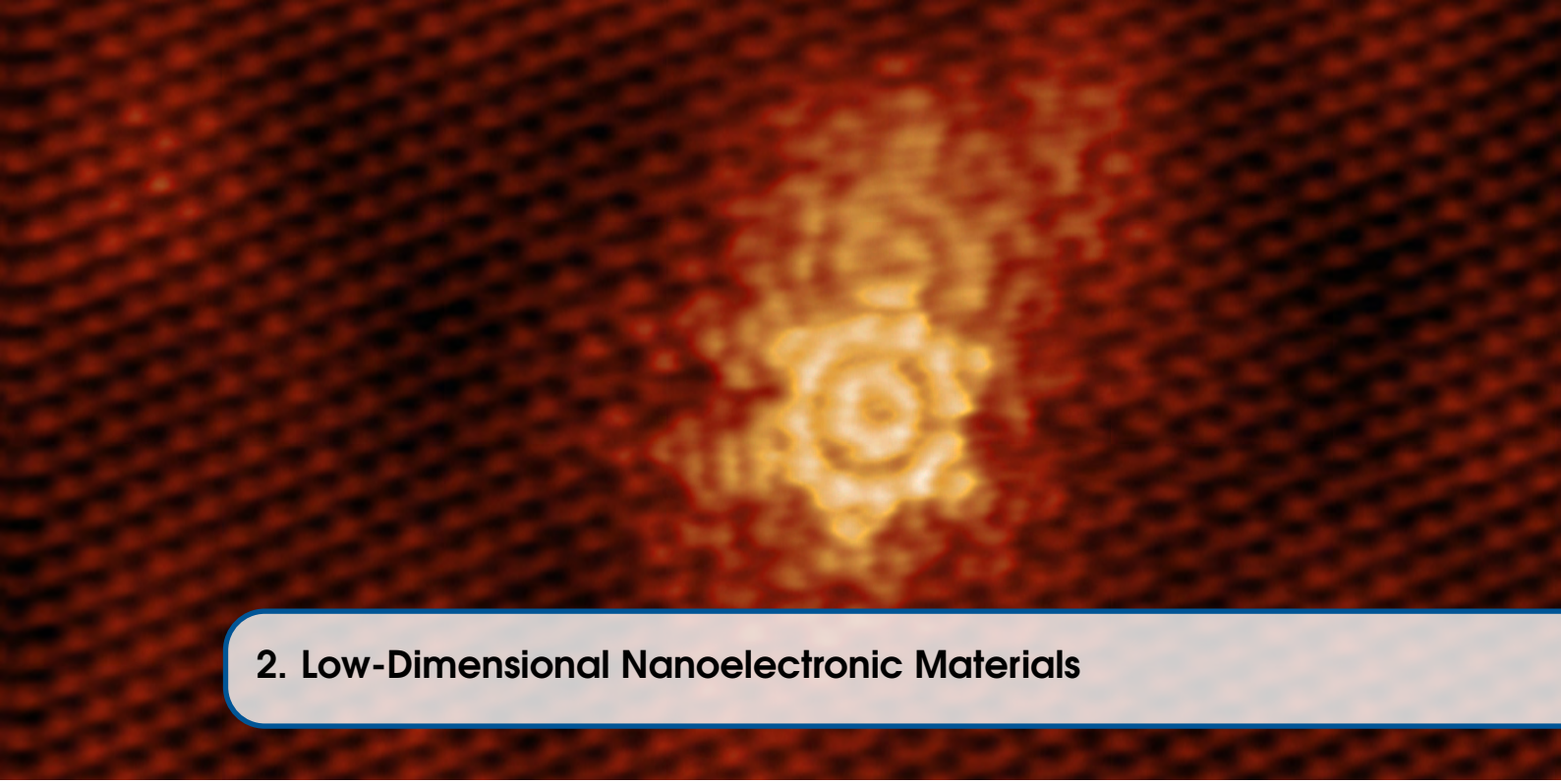


2. Low-Dimensional Nanoelectronic Materials

Mark Hersam (NU), Lincoln Lauhon (NU)

Significance

The Low-Dimensional Nanoelectronic Materials use-case group seeks to understand and realize p-type and n-type doping in the low-dimensional limit. Since low-dimensional nanoelectronic materials have exceptionally high surface area to volume ratios, doping can be realized via two qualitatively different pathways: conventional substitutional doping and surface chemical functionalization. Furthermore, contacts can be designed to selectively inject carriers into the conduction or valence band, thus providing effective n-type and p-type behavior, respectively. Experimental methods in this use-case group include charge transport measurements, optical spectroscopy (e.g., absorbance, photoluminescence, and Raman spectroscopy), and high-resolution microscopy (e.g., scanning probe microscopy, electron microscopy, and atom probe tomography). These experimental methods are complemented by an extensive suite of computational techniques including multi-scale modeling, molecular dynamics, density functional theory, and finite element methods. The interplay between experiment and computation accelerates the understanding and design of doped low-dimensional nanoelectronic materials and their heterostructures.

2.1 Design Goals

The Low-Dimensional Nanoelectronic Materials Use-Case Group is pursuing the following design goals:

Substitutional Doping of Low-Dimensional Semiconductors. Substitutional doping is the most common means of controlling carrier concentration in bulk semiconductors. In the low-dimensional limit, substitutional doping is expected to play the same role, although the reduced degrees of freedom for charge transport suggest that this doping strategy will have greater deleterious effects on charge carrier mobility than in bulk materials. By combining unique characterization methods (e.g., atom probe tomography) with advanced computational methods (e.g., density functional theory), the design trade-offs between

carrier concentration and mobility can be quantitatively understood and exploited to optimize materials properties for low-dimensional nanoelectronic devices.

Surface Chemical Functionalization Doping of Low-Dimensional Semiconductors. Since low-dimensional semiconductors have exceptionally high surface area to volume ratios, carrier concentration can also be controlled via surface chemical functionalization doping. The vast phase space for candidate surface chemical treatments necessitates an MGI-based approach to this design problem. Specifically, electron withdrawing and electron donating chemistries are being screened experimentally and computationally to realize controlled p-type and n-type doping, respectively. The results of this work are informing ongoing efforts to optimize spatially varying doping profiles that serve as the basis of many nanoelectronic devices including p-n junction diodes and transistors.

Developing Heterojunctions Consisting of Low-Dimensional Semiconductors. Since low-dimensional semiconductors have self-passivating surfaces, they can be directly integrated into van der Waals heterostructures without the epitaxial constraints of bulk semiconductors. Since this attribute implies a much greater number of heterojunction possibilities compared to bulk materials, efficient experimental and computational screening methods are required. Specific design goals include engineering of the band alignment and charge/energy transfer across heterojunction interfaces, which will allow optimization of nanoelectronic device metrics such as anti-ambipolarity, operating frequency, and optoelectronic response.

2.2 Significant Accomplishments in 2015

Atomically thin MoS_2/graphene heterostructures are promising candidates for nanoelectronic and optoelectronic technologies. The realization of rotationally commensurate MoS_2 on epitaxial graphene (EG) provides an ideal platform for fundamental studies of low-dimensional heterojunctions and their applications. In addition to the inherent advantages of van der Waals epitaxy (e.g., reduced defect density, sharper interfaces, and consistent material quality), the registry between the MoS_2 and EG allows for the study of crystal orientation-dependent properties as well as specific types of grain boundaries that affect electronic and optoelectronic performance. Towards this end, the crystalline ordering of EG on SiC was exploited to template the growth of monolayer MoS_2 crystal domains by chemical vapor deposition, realizing a transfer-free rotationally commensurate MoS_2/graphene heterostructure with controlled thickness. The rotational ordering of MoS_2 domains observed via local scanning probe microscopy was confirmed to persist over the entire EG substrate by synchrotron X-ray scattering measurements, with preferential alignment of the MoS_2 along the EG lattice direction with matching six-fold symmetry. Electronic characterization of the heterostructure using scanning tunneling spectroscopy revealed a MoS_2 band gap of 2 eV and edge effects leading to band gap narrowing to 0.4 eV in close agreement with DFT calculations. Raman spectroscopy and synchrotron X-ray scattering determined the monolayer MoS_2 to be strain-free. This work was recently published in *ACS Nano* [1].

2.3 Research Accomplishments

Substitutional Doping of Low-Dimensional Semiconductors. The location of substitutional dopants in two-dimensional materials was determined by **Lauhon** using atom probe tomography (APT). Ag-doped $(PbSe)_5(Bi_2Se_3)_3$ was studied due to its tunable interlayer

bonding and previously unknown distribution of dopants between Pb and Bi layers. The APT reconstruction resolved Bi and Pb layers (Figure 2.1a), and spatial distribution maps (Figure 2.1b) indicated that Ag dopants are located in both layers, contrary to the expectation of substitution for Pb alone. Density functional theory calculations by NIST confirms that a distribution of Ag between both layers is energetically most favorable (Figure 2.1c). The precise determination of dopant distribution will advance understanding of how Ag doping changes $(PbSe)_5(Bi_2Se_3)_3$ from a metal to a superconductor. In addition, this work demonstrated the potential for APT to analyze the dopant distribution of two-dimensional materials, especially in the layer-stacking direction. Beyond Ag, Cu-doped Bi_2Se_3 was also analyzed. Cu doping can make Bi_2Se_3 superconducting, but the location of Cu atoms is still under debate. The spatial distribution map of Cu based on APT analysis suggested that Cu atoms are incorporated in both substitutional and intercalated sites (Figure 2.1d). With further refinement, this analysis may elucidate the origin of superconductivity in Cu-doped Bi_2Se_3.

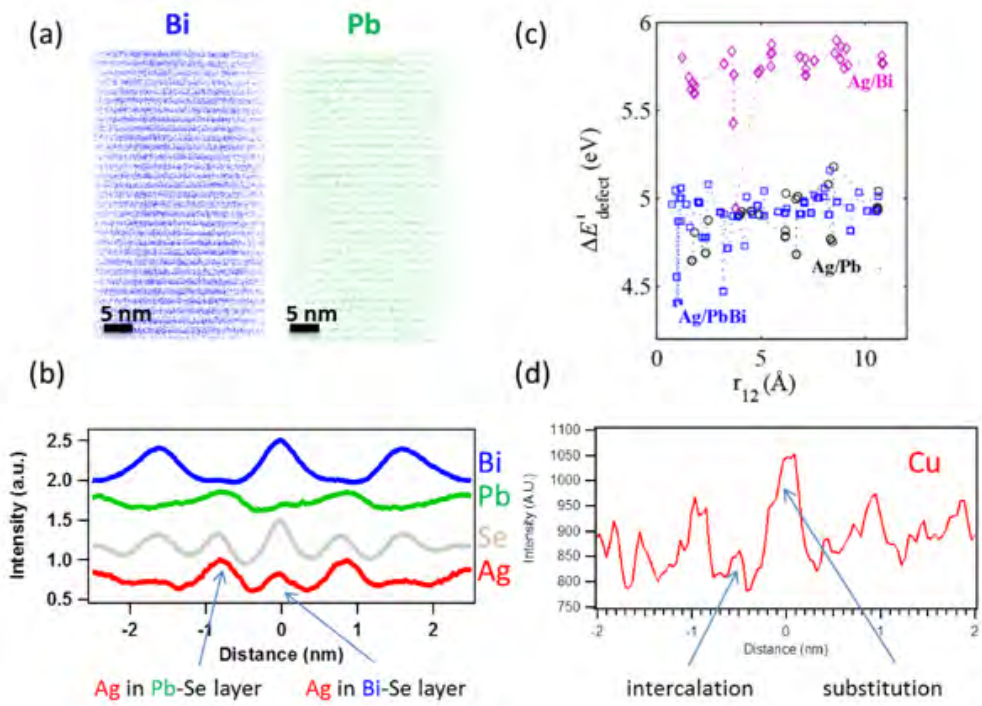


Figure 2.1: (a) A three-dimensional reconstruction of $(PbSe)_5(Bi_2Se_3)_3$ shows layered structures. (b) SDM of Bi, Pb, Se, and Ag relative to Bi. (c) DFT calculation of defect formation energies of Ag in different locations. (d) SDM of Cu relative to Bi in Cu-doped Bi_2Se_3.

Surface Chemical Functionalization Doping of Low-Dimensional Semiconductors. Few-layer black phosphorus (BP) is an emerging two-dimensional nanoelectronic material that possesses a tunable band gap as a function of thickness, high charge carrier mobilities of up to 1000 cm^2/V-s, and highly anisotropic properties. However, BP is chemically reactive and degrades rapidly in ambient conditions. In an inter-use-case group collaboration with **Marks**, **Hersam** has utilized aryl diazonium functionalization for controlled p-type doping of BP. In particular, mechanically exfoliated few-layer BP was covalently functionalized

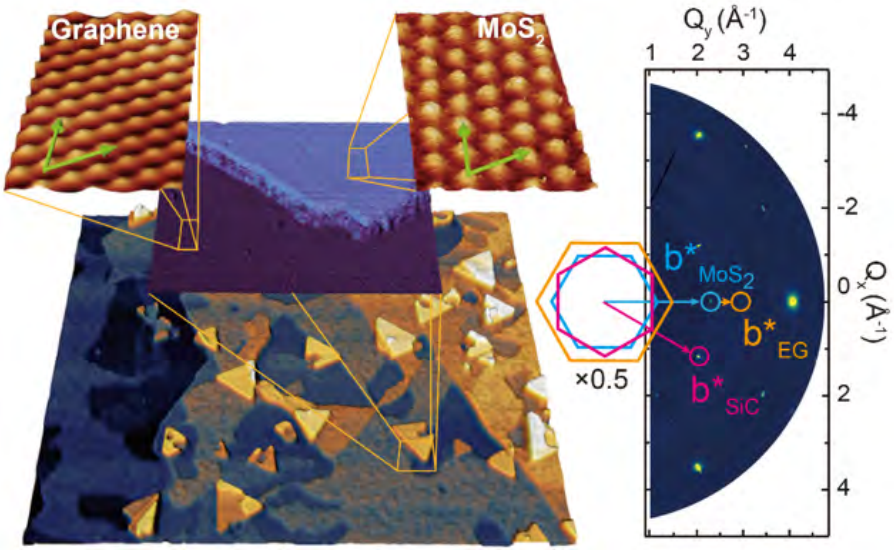


Figure 2.2: AFM height image of MoS_2 crystal domains on EG on SiC. The inset depicts STM atomic resolution images of the graphene and MoS_2. The right panel shows the Qxy 2D reciprocal space map of MoS_2/EG projected from Qz = 0.08 $Å^{-1}$ to 0.12 $Å^{-1}$ by synchrotron X-ray scattering. The b* reciprocal space vectors are indicated by arrows. The MoS_2 and EG vectors coincide, demonstrating rotational alignment of the two materials.

with 4-nitrobenzene diazonium and 4-methoxybenzene diazonium. This chemical modification of few-layer BP results in a controllable p-type doping effect, improving both the BP field-effect transistor device ON/OFF ratio and hole carrier mobility. Furthermore, atomic force microscopy (AFM) measurements demonstrate invariant morphology of the BP after 10 days of ambient exposure, confirming the passivating nature of the diazonium chemistry. The improved stability and tailorable p-type doping of few-layer BP using aryl diazonium functionalization advances its prospects as a low-dimensional semiconductor for nanoelectronic applications.

Developing Heterojunctions Consisting of Low-Dimensional Semiconductors. In an inter-use-case group collaboration with **Bedzyk, Hersam** has realized the synthesis of low-dimensional heterojunctions through the rotationally commensurate growth of atomically thin molybdenum disulfide (MoS_2) on a substrate of epitaxial graphene (EG) on silicon carbide (SiC). The crystalline ordering of the EG substrate was exploited to template the growth of MoS_2 by chemical vapor deposition (CVD), giving rise to a transfer-free two-dimensional heterostructure with registry between its constituent materials (Figure 2.2). The electronic and structural properties of the MoS_2/EG heterostructure were investigated via a comprehensive suite of techniques including AFM, ultra-high vacuum scanning tunneling microscopy and spectroscopy (STM/STS), in situ X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and synchrotron X-ray scattering. In addition to providing an ideal platform for fundamental low-dimensional heterostructure studies, this work suggests that EG is a promising substrate for the van der Waals epitaxial growth of other emerging two-dimensional nanoelectronic materials.

2.4 Collaborations

2.4.1 CHiMaD Collaborations

Anti-Ambipolar Semiconductor Heterojunctions
*Tobin **Marks** (NU), Lincoln **Lauhon** (NU), and Mark **Hersam** (NU)*
Gate-tunable p-n junctions are realized from semiconductor heterojunctions. These devices show anti-ambipolar transfer curves. This work resulted in the following collaborative publication, [2].

Rotationally Commensurate Growth of MoS_2 on Epitaxial Graphene
*Michael **Bedzyk** (NU), Mark **Hersam** (NU)*
Rotationally commensurate growth of MoS_2 on epitaxial graphene is realized via chemical vapor deposition. This work resulted in the following collaborative publication, [1].

2.4.2 NIST Collaborations

FET Fabrication and Characterization of $MoTe_2$ 2H and 1T Bulk Crystal Samples
*Albert Davydov (NIST), Mark **Hersam** (NU), Francesca Tavazza (NIST), Arunima Singh (NIST)*
Davydov has developed a CVT sysnthesis of both 2H and 1T phases of $MoTe_2$. **Hersam** is mechanically exfoliating these bulk crystals, fabricating FETs, and performing transport measurements to confirm the semiconducting and metallic nature of the 2H and 1T phases, respectively. Tavazza and Singh are providing computational support for this effort.

Effect of MoS_2 Stoichiometry on Morphology of MoS_2 Flakes During Growth
*Lincoln **Lauhon**, Francesca Tavazza (NIST), Arunima Singh (NIST)*
The effect of Mo/S availability during MoS_2 growth on the resulting MoS_2 crystal shape is being investigate by Singh and Tavazza using first-principles simulations. This work complements **Lauhon** et al. effort on CVD growth of MoS_2 providing interpretation of its results. Energetic evaluations of island of different shapes have been conducted, as well as corresponding determination of charge rearrangement and vacancy formation energy. Density of state analysis of the many investigated configurations is currently ongoing.

Device Fabrication and Testing of Large-area MoS_2 Thin Films
*Mark **Hersam** (NU), Lincoln **Lauhon** (NU), Albert Davydov (NIST)*
Hersam and **Lauhon** have recently published work on the memristive behavior of sub-stoichiometric monolayer MoS_2 with grain boundaries. The highly polycrystalline nature of the NIST MoS2 thin films fabricated from sulfurization of MoO_3 by Davydov may allow for large-scale fabrication of gate-tunable memristors. **Hersam** is fabricating FETs using the Davydov MoS_2 films and checking for the presence of bi-stable switching at high source-drain bias.

First Principles Calculations of Doping in Layered Compounds
*Lincoln **Lauhon** (NU), Francesca Tavazza (NIST), Arunima Singh (NIST)*
First-principles simulations were performed by Singh and Tavazza to complement the efforts of **Lauhon** et al. to map the location of substitutionally doped Ag atoms in $(PbSe)_5(Bi_2Se_3)_{3m}$(m = 1,2,...), a homologous series of compounds consisting of 2D heterostructures of Bi_2Se_3 layers and PbSe layers. First principles simulations of defect formation energy and temperature dependent probabilities of an ensemble of substitutionally doped Ag-$(PbSe)_5(Bi_2Se_3)_3$ reveal that the Ag exists predominantly in both PbSe layers and Bi_2Se_3 layers up to temperatures as high as 1000 K. The computational results agree well with ATP measurements, both confirming that Ag exists in both PbSe layers and

Bi_2Se_3 layers. In future, such symbiotic experimental and computational investigations can be used for accurate determination of dopant locations in 2D materials; revealing structure-property relations and resulting in the development of controlled growth techniques for engineering materials properties.

Chemical Vapor Transport Growth of Transition Metal Dichalcogenides and Alloys
*Lincoln **Lauhon** (NU), Albert Davydov (NIST), Sergiy Krylyuk (NIST)*
Upon request from the **Lauhon** group, Davydov and Krylyuk have grown a set of single-crystalline transition metal dichalcogenides (TMDC) platelets, including $MoTe_2$ and WTe_2 crystals grown by chemical vapor transport. The **Lauhon** group is currently testing these TMDC crystals to design the sample-prep methodology suitable for analysis using atom probe tomography at Northwestern University. Additional collaboration on synthesis and characterization is planned.

2.4.3 External Collaborations

Anti-Ambipolar Semiconductor Heterojunctions
*Mark **Hersam** (NU), Chris Kim (University of Minnesota)*
Gate-tunable p-n junctions are realized from semiconductor heterojunctions. These devices show anti-ambipolar transfer curves. This work resulted in the following collaborative publication, [2].

Doping Black Phosphorus via Chemical Modification
*Mark **Hersam** (NU), George Schatz (NU)*
Two-dimensional black phosphorus is realized via functionalization with diazonium chemistry. This work is currently being prepared for publication: C. R. Ryder, J. D. Wood, S. A. Wells, Y. Yang, D. Jariwala, T. J. Marks, G. C. Schatz, and M. C. Hersam, "Covalent functionalization and passivation of exfoliated black phosphorus via aryl diazonium chemistry," in preparation, 2015.

Growth of Ag doped (PbSe)5(Bi2Se3)3 and Cu doped Bi_2Se_3
*Lincoln **Lauhon** (NU), Mercouri Kanatzidis (NU)*
Kanatzidis group provides samples of Ag doped $(PbSe)_5(Bi_2Se_3)_3$ and Cu doped Bi_2Se_3. **Lauhon** group is characterizing these layered 2D materials using atom probe tomography to study the influence of interlayer bonding strength.

2.5 Technology Transfer

Invention
System and method for anti-ambipolar heterojunctions from solution-processed semiconductors
D. M. Jariwala, V. K. Sangwan, W. Xu, H. Kim, T. J. Marks, M. C. Hersam
U.S. Provisional Patent application filed on 1/9/15
Patent Number: 62/101, 676
This invention describes a method for forming large-area, anti-ambipolar p-n heterojunctions using solution-processed p-type semiconducting single-walled carbon nanotubes (s-SWCNTs) and n-type amorphous indium gallium zinc oxide (a-IGZO) thin films via photolithographic and etching techniques

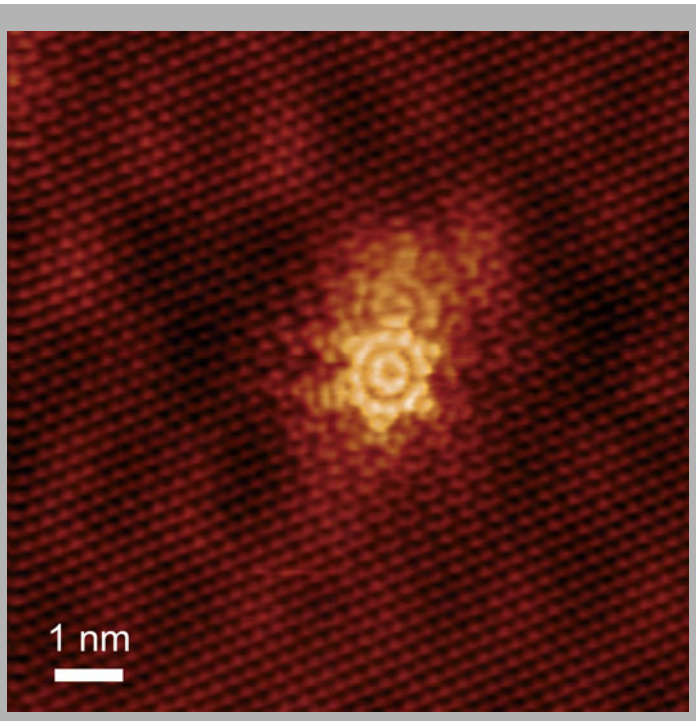
2.6 Publications and Presentations

2 Number of CHiMaD-supported publications in 2015 by Low-Dimensional Nanoelectronic Materials use-case group. Please see chapter 20 for details. [1, 2]

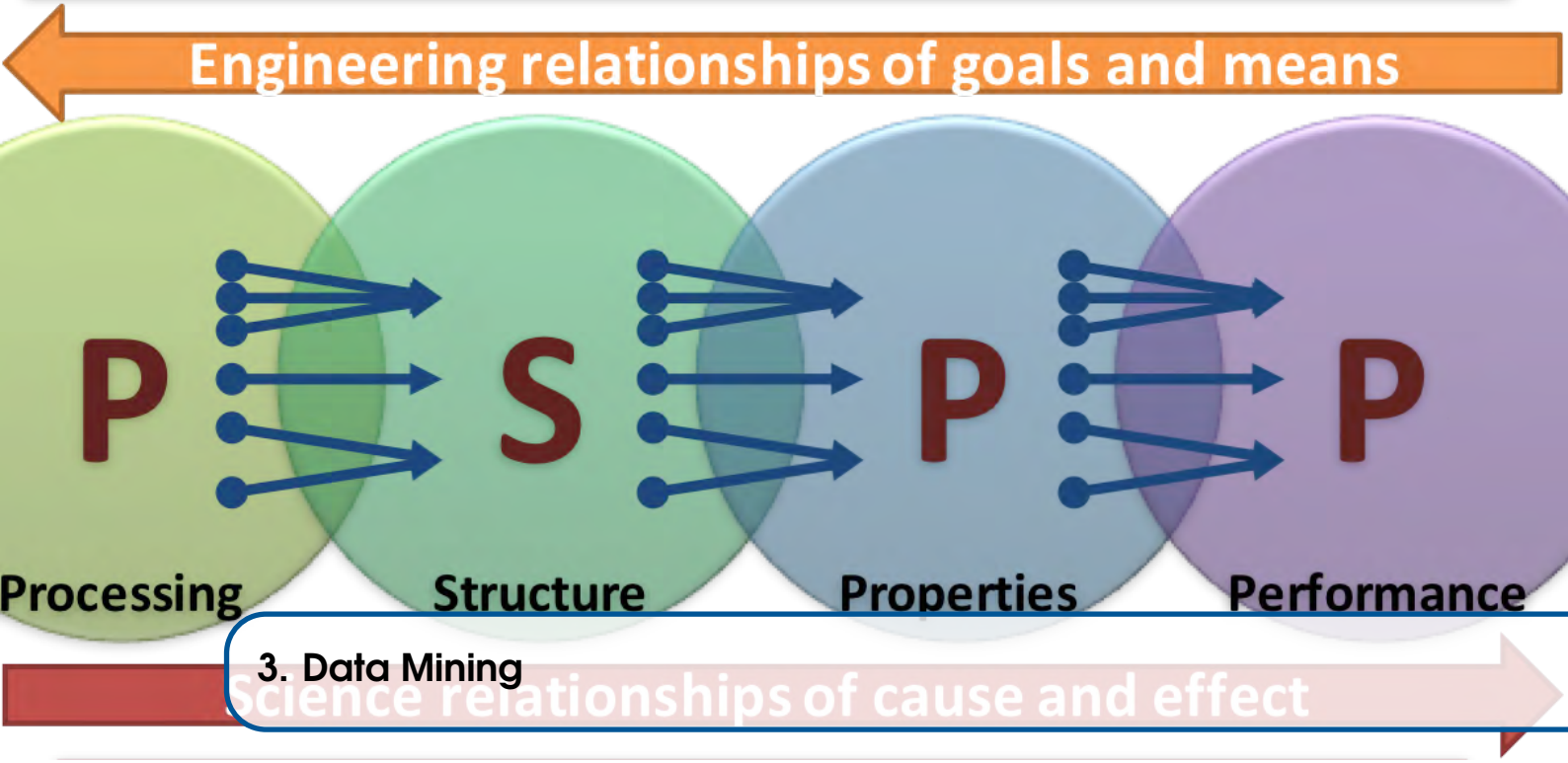
25 Number of presentations on CHiMaD supported research in 2015, please see section 21.1 for the complete list.

2.7 CHiMaD Team

Low-Dimensional Nanoelectronic Materials Use-Case Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Mark Hersam	Principal Investigator	NU/MSE	
Lincoln Lauhon	Principal Investigator	NU/MSE	
Hadallia Bergeron	Graduate Student	NU/MSE	Low-dimensional semiconductor heterojunctions *(Hersam)*
Xiaochen Ren	Graduate Student	NU/MSE	Substitutional doping and alloy formation in transition metal dichalcogenides *(Lauhon)*



Header Image: Ultra-high vacuum scanning tunneling microscopy image of epitaxial graphene, which is used as a growth substrate for MoS_2. Figure adapted from reference [1]



3. Data Mining

Alok Choudhary (NU), Ankit Agrawal (NU), Gregory Olson (NU), Chris Wolverton (NU), Wei Chen (NU)

Significance

The CHiMaD data mining team is working towards making significant advances in data-driven informatics to accelerate materials discovery. In this era of big data, we are being bombarded with huge volumes of data from a variety of different sources (experiments, simulations) at unprecedented rates in practically all fields of science and engineering, and materials science is no exception. Advanced techniques for data-driven analytics are needed to analyze all this data in ways that can help extract meaningful information and knowledge from it, and thus contribute to accelerating materials discovery and the vision of Materials Genome Initiative. The diversity and expertise within the CHiMaD team provides unique opportunities for collaborations among materials scientists and computer scientists to realize this goal. This requires designing and developing specific analytics and data mining approaches for problems in materials science, and evaluating the resulting insights/discoveries via necessary experiments and simulations. The long-term vision is to work with NIST to enable data-to-discovery (or actionable insights) at unprecedented latency through summary statistics, query, reporting, analysis, bottom-up as well as hypothesis-driven discoveries and data mining on various heterogeneous and big databases that are complex, high dimensional, structured and semi-structured.

3.1 Design Goals

The design goals of the Data Mining use-case group for this reporting period were three-fold:

- Continue to make progress in the materials informatics projects started last year
- Initiate new projects within those collaborations where possible
- Explore other important problems in materials science that can benefit from data-driven informatics, and try to kick-off new collaboration(s) both within and outside the CHiMaD team, and also with NIST researchers.

The ongoing projects from last year include our efforts towards integrating CALPHAD and data mining for predicting the fatigue strength of steel for advanced steel design, identifying significant microstructure descriptors for microstructure representation and design, and extending our composition-based machine learning framework to computationally discover new materials with desired properties. Further, we have started a new project in which we try to take into account the characteristics of the crystal structure in addition to composition information, for the purpose of predicting properties of materials. This year we have also started a new collaboration with NIST researchers that aims at automating the currently-manual process of classification of journal articles as being relevant or not relevant for NIST's Thermodynamic Research Center (TRC) team to extract key data from it, as part of their data curation effort. Finally, we have recently embarked upon discussions with the CHiMaD OPV use-case group for a potentially new collaboration exploring the use of data mining to design and develop organic photovoltaics, and are currently looking to find an appropriate dataset to kick-off our data mining efforts in this arena.

3.2 Significant Accomplishments in 2015

Improved Prediction of Fatigue Strength of Steel. The team of **Agrawal, Choudhary, Olson,** and Xiong (NU) have integrated a steel process-property database from NIMS with CALPHAD database, and constructed accurate predictive models for fatigue strength of steel which are more widely applicable than prior models based on process and composition.

Framework for Discovery of New Metallic Glasses. In collaboration with **Agrawal, Choudhary, and Wolverton,** Ward (NU) has further developed composition-based machine learning framework to computationally discover new metallic glasses.

Improved Microstructural Descriptors. In collaboration with **Chen** and Dan Apley (IEMS department, NU), Zhang (NU) has developed a Structural Equation Modeling (SEM) approach to identify significant microstructure descriptors for microstructure characterization and reconstruction.

Improved Prediction of Formation Energy of New Compounds. In collaboration with **Agrawal, Choudhary, and Wolverton,** Ward (NU), Liu (NU), Krishna (NU), and Hegde (NU) have developed a technique based on Voronoi tessellations to incorporate the crystal structure in the machine learning model for predicting the formation energy of new compounds.

Development of Accurate Topic Modelling-based Classifier. A new collaboration between **Agrawal, Choudhary,** Krishna (NU), and NIST researchers Dima (NIST), Kroenlein (NIST), Padi (NIST), and Peskin (NIST), has developed an accurate topic modeling based classifier for scientific journal articles to support the ongoing data curation effort at the NIST Thermodynamic Research Center.

3.3 Research Accomplishments

Integrating CALPHAD and Data Mining for Advanced Steel Design. This work involving a collaboration of **Agrawal, Choudhary, Olson,** and Xiong(NU), aims to design an effective interface between data mining technique and CALPHAD methodology for materials genomic design. The research studies are performed on the carbon steels fatigue strength data with raw data sets obtained from experiments provided by NIMS (National Institute

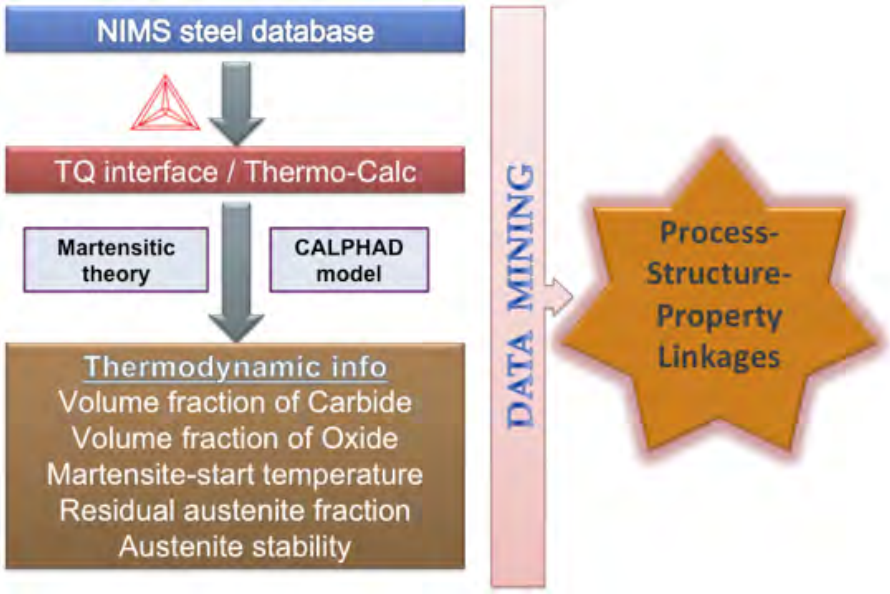


Figure 3.1: Overall schematic of the integration of NIMS process-property database and CALPHAD modeling, and extracting process-structure-property linkages.

for Materials Science, Japan). The CALPHAD method is widely adopted as one of the most powerful tools for designing new materials and processing heat treatment. Therefore, it is critical to further develop CALPHAD method to study process-structure-property relationships. As a start, data-mining model and CALPHAD database were coupled using the in-house code through TQ-interface in the Thermo-Calc software package (Figure 3.1). The machine learning process indicated that martensite-start (Ms) temperature is the most critical parameter among the five thermodynamic parameters. Therefore, this year a new model for calculating Ms temperature was investigated based on statistical analysis on experimental databases, which takes less elemental influence into account. It was found that the new model not only gives better estimates of Ms temperature but also in turn of fatigue strength, which is quite promising and further approves the sensitivity of Ms temperature for fatigue resistance. CALPHAD based data mining models gave excellent prediction accuracy for fatigue strength with R^2 values of around 0.9, which although is lower than prior models, has the advantage of not being directly dependent of composition parameters, and thus are more widely applicable for new steel compositions. A manuscript on this work is in-preparation.

Composition-based Machine Learning Framework for Predicting Inorganic Material Properties. This collaboration between **Agrawal, Choudhary, Wolverton,** and Ward (NU) aims at creating an extensive set of composition-based parameters of materials that could be coupled with data mining to effectively predict a wide variety of material properties. Building upon our efforts from last year, we have focused this year on using our composition-based machine-learning framework to predict new materials, in particular metallic glass alloys, which possess a unique blend of properties from both metallic and amorphous materials. For training the machine learning model, we used experimental measurements taken from *Nonequilibrium Phase Diagrams of Ternary Amorphous Alloys'* a volume of the Landolt-Börnstein collection. A machine learning model was created to predict whether it is possible to form a metallic glass alloy at a certain composition using melt spinning. Without any specific modifications for metallic glasses, we found that

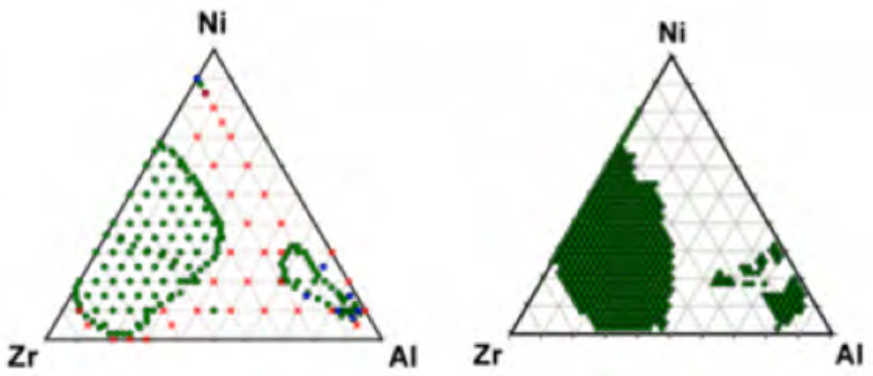


Figure 3.2: (left) Experimentally-measured regions of glass-forming ability in the Al-Ni-Zr ternary system. (right) Predicted glass-forming ability by a machine learning model that was trained without any data from the diagram present on the left.

models created using our framework are 90% accurate in cross-validation tests. To further evaluate the ability of the model to extrapolate to new alloy systems, we devised a test where we intentionally omitted an entire phase diagram from the training data and then evaluated the performance of the model in that system. As shown in Figure 3.2, a machine learning model trained without any data from the Al-Ni-Zr ternary system could accurately predict the existence, locations, and relative sizes of the two glass-forming regions. This result makes us confident that we can use this model to evaluate new chemical systems. This framework has also been shown to be effective in predicting band gap of a compound, which is crucial for discovery of semiconductor materials. A manuscript on this work is in-preparation.

Supervised Learning-based Microstructure Characterization and Reconstruction. In collaboration with **Chen** and Daniel Apley (IEMS department, Northwestern University), Zhang (NU) has developed a Structural Equation Modeling (SEM) approach to identify significant microstructure descriptors with the least dependency. The method addresses descriptor redundancy in the existing approach and provides insight into the underlying latent factors for categorizing microstructure. The effectiveness of the approach is demonstrated and validated through confirmation of the reconstructed images and simulated material properties of the epoxy-nanosilica system.

Fast Models for Properties of Crystalline Compounds Using Voronoi Tessellations and Machine Learning. This is a collaborative work between **Agrawal, Choudhary, Wolverton,** and Ward (NU), Liu (NU), Krishna (NU), and Hegde (NU), where the goal is to effectively incorporate crystal structure information into machine learning models to predict material properties. The technique involves the use of Voronoi Tessellations to define the nearest neighbors of each atom, and then evaluating characteristics such as the coordination number and the difference in elemental properties between the atom and its neighbors. Subsequently attributes are created that describe the entire crystal by computing statistics of the distribution of local environments over all atoms. The final step is to employ machine learning to link these attributes to the property of the material. The first application for this technique has been to predict the formation energy of crystalline compounds using data from the OQMD. We have benchmarked our technique against two other machine learning approaches and found that our models can be about twice as accurate (Figure 3.3).

Classification of Scientific Journal Articles to Support NIST Data Curation Efforts This

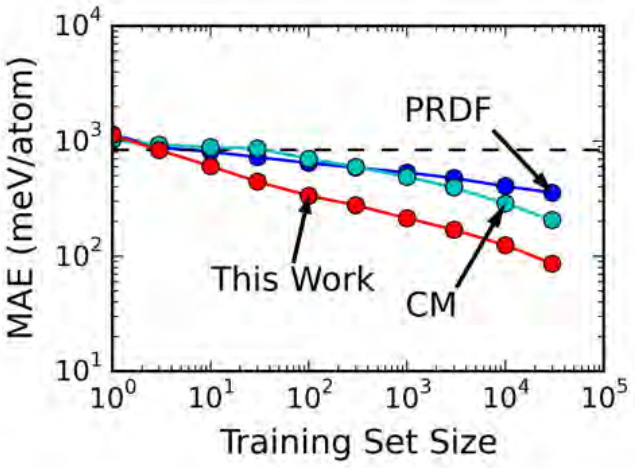


Figure 3.3: Comparison of the accuracy (in terms of error) of the Voronoi-tessellation-based technique we are developing to the Coulomb Matrix (CM) [Int. J. Quantum Chem. 115, 1094 (2015)] and Partial Radial Distribution Function (PRDF) [Phys. Rev. B 89, 205118 (2014)] approaches. Our model predicts the formation energy of crystalline compounds about twice as accurately as these approach for most training set sizes.

new collaboration between **Agrawal, Choudhary,** Krishna (NU), and NIST researchers Dima (NIST), Kroenlein (NIST), Padi (NIST), and Peskin (NIST), is aimed at supporting the data curation effort of the NIST Thermodynamic Research Center (TRC). Its current curation process is largely manual that requires each journal article to be examined and evaluated for relevance before trying to extract data from it. In the current work, a topic modeling based binary classifier was developed using a corpus of 2357 articles where the relevancy of the article was manually pre-assigned. Out of 2357 articles, 1172 were relevant, and 1185 were not relevant. Topic modeling was done based on LDA (Latent Dirichlet Allocation) with hyper parameter optimization. The resulting topics were used as a training set for machine learning algorithms capable of doing binary classification. The best cross-validation accuracy obtained, in terms of area under the ROC curve, was 0.95 on 2357 articles dataset with 1000 topics (for each article). Further, an online tool deploying the classifier is under construction (beta version available at: http://info.eecs.northwestern.edu/TRCArticleClassifier).

3.4 Collaborations

3.4.1 CHiMaD Collaborations

Data Mining for Design and Development of OPV Materials

*Ankit **Agrawal** (NU), Alok **Choudhary** (NU), Christopher **Wolverton** (NU), Luping **Yu** (UC), Guilia **Galli** (UC)*

During the *CHiMaD Materials Design Workshop I* use-case presentation by Goldey (UC) and Schneider (UC), a possible collaboration between the Organic Bulk Heterojunction Polymer Solar Cells and Data Mining use-case groups came to light. After initial discussions between use-case groups including Goldey (UC), Schneider (UC), Ward (NU), Furmanchuk (NU), Paul (NU), it was decided that there is little correlation between device efficiency and energy levels of polymeric material, but stronger correlations between power

conversion efficiency and morphology-dominated properties.The groups will be exploring the possibility of using data mining for determining the uncontrolled morphology of active layer in order to support building of OPV devices. See section **??** for more details.

3.4.2 NIST Collaborations

Classification of Scientific Journal Articles to Support NIST Data Curation Efforts
*Ankit **Agrawal** (NU), Alok **Choudhary** (NU), Alden Dima (NIST), Kenneth Kroenlein (NIST), Sarala Padi (NIST), Adele Peskin (NIST)*
This collaboration is aimed at supporting the data curation effort of the NIST Thermodynamic Research Center (TRC) by classifying an article as relevant or not relevant to their data extraction pipeline. An online tool deploying the classifier is under construction (beta version available at: http://info.eecs.northwestern.edu/TRCArticleClassifier)

3.4.3 External Collaborations

Structural Equation Modeling
*Wei **Chen** (NU), Dan Apley (NU)*
Through this collaboration, **Chen** and Apley are developing the supervised based learning algorithm for microstructure characterization and reconstruction.

3.5 Technology Transfer

Software/Web-Tool
TRC Article Classifier
A. Khrishna, A. Agrawal, A. Choudhary
Access Link (Beta): http://info.eecs.northwestern.edu/TRCArticleClassifier
This is a software tool deploying the models for classfying a journal article as relevant or not relevant to NIST Thermodynamics Research Center's ongoing data curation efforts. It is based on unsupervised topic modeling followed y supervised classification.

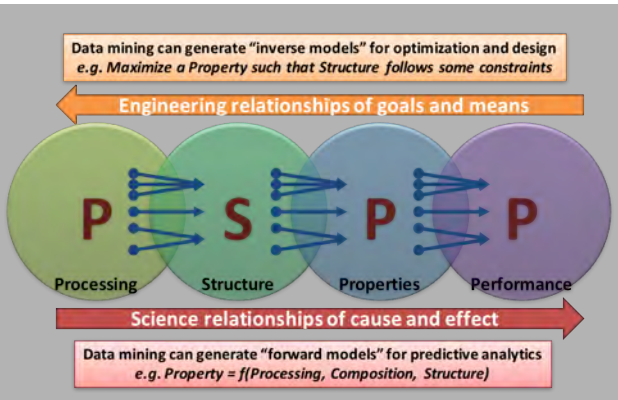
Software
Materials Agnostic Platform for Informatics and Exploration (Magpie)
L. Ward, C. Wolverton
Access Link (Beta): https://bitbucket.org/wolverton/magpie
Magpie is a software package designed to simplify the process of using machine learning to develop new materials. This software includes the ability to compute attributes of materials, train and validate models, and predict the properties of new materials all through a simple command-line interface. Magpie also makes it possible to share results with other research groups by creating interactive webpages or saving models in a system independent format.

3.6 Publications and Presentations

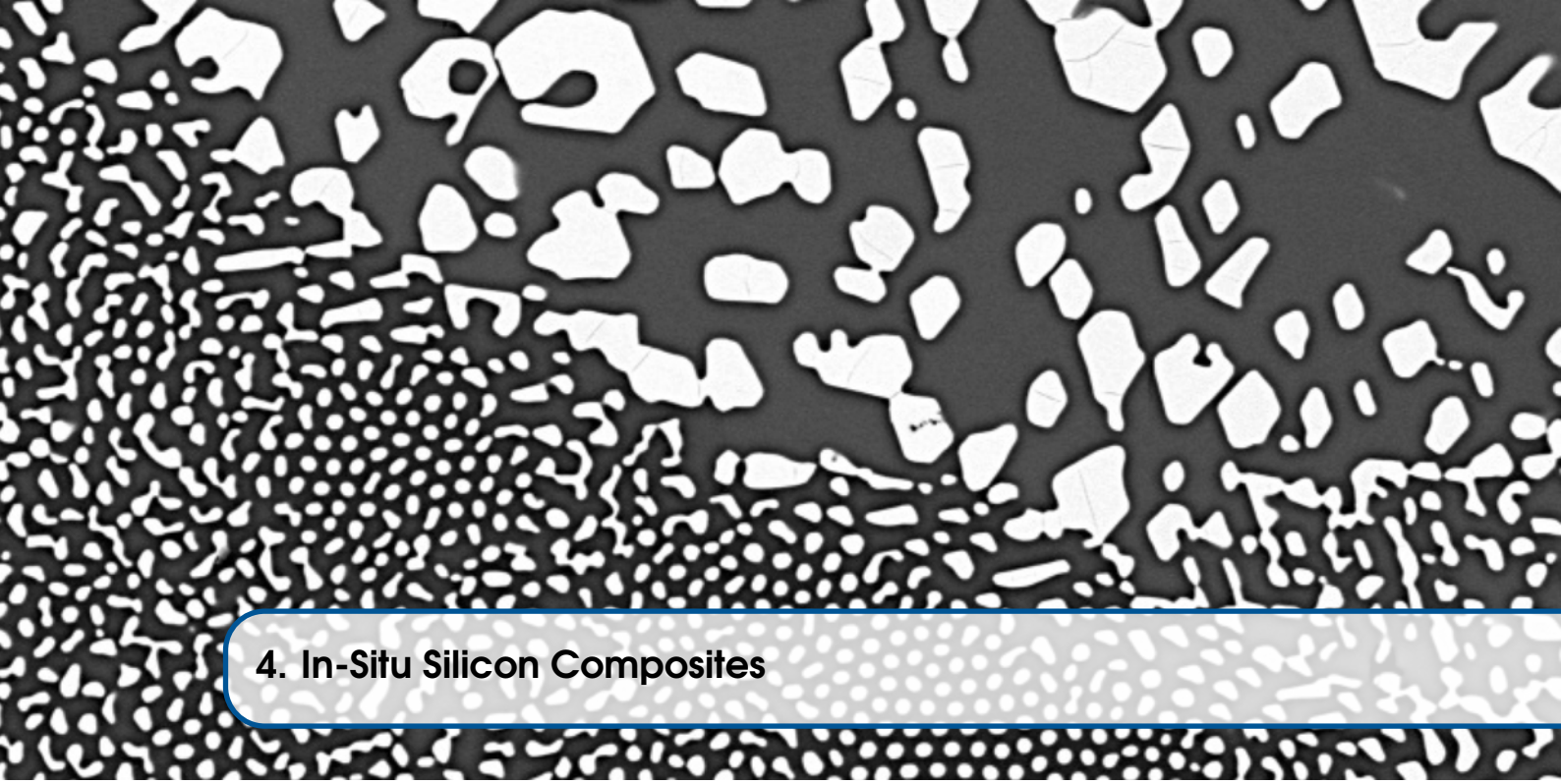
11 Number of presentations on CHiMaD supported research in 2015, please see section 21.2 for the complete list.

3.7 CHiMaD Team

Data Mining Use-Case Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Alok Choudhary Ankit Agrawal Gregory Olson Christopher Wolverton Wei Chen	Principal Investigator Principal Investigator Principal Investigator Principal Investigator Principal Investigator	NU/EECS NU/EECS NU/MSE NU/MSE NU/ME	
Wei-keng Liao	Research Faculty	NU/EECS	*(Choudhary, Agrawal)*
Wei Xiong	Research Associate	NU/MSE	CALPHAD Databases *(Olson)*
Al'ona Furmanchuk	Research Associate	NU/EECS	Data mining for design and development of OPV Materials *(Choudhary, Agrawal)*
Amar Krishna	Graduate Student	NU/EECS	Fast models for properties of crystaline compounds using Voronoi tessalation and machine learning *(Choudhary, Agrawal)*
Rouqian Liu	Graduate Student	NU/EECS	Fast models for properties of crystaline compounds using Voronoi tessalation and machine learning *(Choudhary, Agrawal)*
Arindam Paul	Graduate Student	NU/EECS	*(Choudhary, Agrawal)*
Logan Ward	Graduate Student	NU/MSE	Machine Learning for Materials Discovery *(Wolverton)*
Yichi Zhang	Graduate Student	NU/ME	Microstructure Characterization and Reconstruction *(Chen)*



Header Image: Datamining chart provided by (Agrawal).



4. In-Situ Silicon Composites

Peter Voorhees (NU), Christopher Wolverton (NU)

Significance

One of the major objectives of the CHiMaD is to transfer the knowledge of materials design to industry. In support of this goal, the Si-alloys use-case group was undertaken in close partnership with the Dow-Corning Corporation. The collaboration with Dow Corning scientists was very close, with a significant number of the use-case group members at Dow Corning. During the course of this work the in-situ Silicon Composites use-case group: established CALPHAD databases relevant to the design of these materials, showed that ab-initio molecular dynamics can be used to provide accurate liquid diffusion coefficients in these high temperature alloys and to create a liquid diffusion database, developed a new model for eutectic solidification in multicomponent alloys that employed the CALPHAD and liquid diffusion databases, developed a molar volume database that was used successfully to design alloys that minimized cracking upon solidification, and showed that Sr additions alone do not alter the morphology of the Si plates found in Si-Cr eutectics thus establishing that the classical model for effects of Sr on Si-plate morphology does not hold. These databases and models were combined with proprietary casting codes and Dow-Corning databases to predict the microstructure of Si castings. Unfortunately, Dow Corning decided to discontinue the Si alloys project, and thus we will be ending the Si-alloys use-case group in CHiMaD.

4.1 Design Goals

The over-arching goal of the project is to the design of melt-castable ceramic materials, and to design high performance Si-based composite materials for structural applications. The focus of the use-case group is on Si-Cr-Ti-Co alloys. A major challenge with these materials is that the Si is a strong compound former. Since both Si, at room temperature, and Si compounds are brittle phases, the challenge is to design a polyphase microstructure that increases the toughness of the materials beyond that of the constituent phases. Thus, CALPHAD modeling is needed to choose the alloy compositions and predict the phases

present for a given alloy composition. The required toughness of the composite can be attained through a fine spatial dispersion of one brittle phase in another. This polyphase mixture should have microstructural features sufficiently small, and thus interfacial area sufficiently high, to yield significant crack deflection. Such crack deflection is well known to yield a tough material using brittle component phases. The fine distribution of the phases will be created via solidification of eutectic or near-eutectic alloys. Thus, models of the eutectic solidification process are needed to design the processing path and molds to yield these fine microstructures. Finally, since Si expands on freezing, it is necessary to choose alloy compositions that minimize solidification induced cracking. The goal is to produce to produce a castable-ceramic with a toughness in the 4-6 MPa $m^{1/2}$ range.

4.2 Significant Accomplishments in 2015

Eutectic Growth in Two-Phase Multicomponent Alloys. A theory of two-phase eutectic growth for a multicomponent alloy has been formulated. Using the local equilibrium hypothesis, a theory for eutectic growth of an alloy with N elements has been developed. We show that the growth law determined by Jackson and Hunt for binary eutectics can be generalized to alloys with N elements. We find that the spacing of the eutectic for a given interfacial velocity can be changed dramatically with the addition of a slow diffusing element, or if the slope of the liquidus of the ternary addition is different from that of the binary elements, see Figure 4.1. All of the quantities necessary to determine the change in the eutectic spacing can be derived from a CALPHAD model of the multicomponent thermodynamics.

We now have a model that can be used to guide the design of multicomponent alloys to yield a given eutectic lamellar spacing. The spacing of the lamellar is a key factor in setting the properties of eutectic alloys. A detailed publication is under preparation.

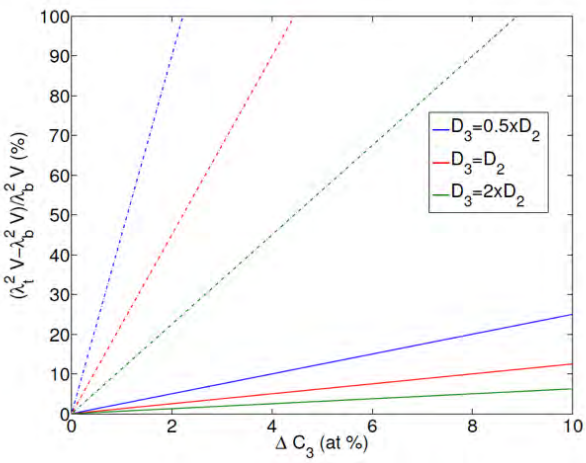


Figure 4.1: The variation of the product of the spacing of the eutectic microstructure λ_t and the interfacial velocity V with the addition of element 3 compared to that of the symmetrical binary alloy λ_b.ΔC_3 is the difference in concentrations of component 3 between the two solid phases, α and β. Dashed lines correspond to: $m_3^\beta = -9K/(at\%), m_3^\alpha = -10K/(at\%)$, solid lines correspond to: $m_3^\beta = 10K/(at\%)$ and $m_3^\alpha = -10K/(at\%)$,, where m_i is the slope of the liquidus due to component i of the noted phase. The addition of the slow diffusing element can have a large effect on the eutectic spacing for a given interfacial velocity.

4.3 Research Accomplishments

This past year we have created three databases: A CALPHAD database for Si-Cr-Co and Si-Ti-Co alloys, a liquid diffusion database derived from abinitio molecular dynamics, and a molar volume database for ternary and higher order alloys that is derived from density functional calculations. The experimental data supplemented with the AIMD calculations provided parameters to calculate the liquid molar volume of the multi-component Si-Cr-Co-Ti over a large range of temperatures and compositions. The molar volume database was employed to mitigate the effects of the expansion of the Si during solidification. Using this database and the CALPHAD database in a Scheil-Gulliver model for solidification, alloy compositions were chosen that yield a molar volume of the last-to-solidify liquid that is similar to that in the solid. Initial calculations in the Si-Cr-Al system matched the experimental data from Dow Corning, confirming that this approach can be used to design alloys that minimize solidification induced fracture. In addition, we have developed a model for two-phase multicomponent eutectic growth. The model can be used to predict, for example, the dependence of the eutectic spacing on the addition of a ternary alloying element to a binary alloy. This model uses the the CALPHAD and liquid diffusion databases. In an effort to develop a more isotropic eutectic morphology, the effects of small additions of Sr on the morphology of the Si phase in the Si-Cr eutectic was examined. The results of experiments performed at DCC were quite surprising. Unlike past work, the Sr had little effect on the morphology of the Si plates in the eutectic. This finding indicates that Sr alone does not affect the growth of the facetted Si phase. The changes in morphology that have been reported in the literature must therefore be due to some other effect, such as the presence of both Al and Sr in the alloy. This past year we also began work on a phase field crystal model for solidification with the highly anisotropic solid-liquid interfacial energies. These highly anisotropic interfacial energies can lead to the facetted microstructures observed in Si alloys.

4.4 Collaborations

4.4.1 NIST Collaborations

CALPHAD Assesment of Si Alloys
*Ursula Kattner (NIST), Peter **Voorhees**(NU)*
Voorhees group collaborated with Kattner, an expert on CALPHAD assesment of phase equilibria, for CALPHAD assesment of Si alloys.

Phase Field Model Development
*James Warren (NIST), Peter **Voorhees**(NU)*
Voorhees group collaborated with Warren on model development.

4.4.2 External Collaborations

In-situ Si Composites
*Peter **Voorhees** (NU), Vasgen Shamamian (Dow-Corning), Kwon Skinner (Dow-Corning), Andres Becerra (Dow-Corning), Lance Wu (Dow-Corning)*
Voorhees group closely collaborated with Si-alloys group at Dow-Corning for this project.

4.5 Publications and Presentations

3 Number of presentations on CHiMaD supported research in 2015, please see section 21.3 for the complete list.

4.6 CHiMaD Team

In-Situ Si Composites Use-Case Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Peter Voorhees	Principal Investigator	NU/MSE	
Christopher Wolverton	Principal Investigator	NU/MSE	
Nana Ofori-Opoku	NIST-CHiMAD Postdoc	NU-NIST	*(Voorhees, Warren)*
Oriane Senninger	Postdoctoral Researcher	NU/MSE	*(Voorhees)*
Shiqiang Hao	Postdoctoral Researcher	NU/MSE	*(Wolverton)*
Matthew Peters	Graduate Student	NU/MSE	*(Voorhees)*

5. Directed Self-assembly of Block Copolymer Films for Lithography

Paul Nealey (UC), Juan de Pablo (UC), Steven Sibener (UC), Luping Yu (UC), Heinrich Jaeger (UC), Ian Foster (UC/ANL)

Significance

Directed self-assembly (DSA) of block copolymers (BCPs) has the potential to revolutionize nanomanufacturing. BCPs self-assemble to form densely packed features with highly uniform dimensions and shapes in ordered arrays at the scale of 3 to 50 nm. Chemical pre-patterns or templates may be defined using traditional lithographic materials and processes such as 193 immersion lithography at the scale of 80 nm. By directing the assembly of block copolymer films on the templates, the overall resolution of the lithographic process may be increased by three to four-fold or more and still meet the stringent requirements of manufacturing, including perfection, dimension control, and pattern placement accuracy. The interest and exponential growth in research activity and expenditure is driven in the semiconductor industry by the prospect of manufacturing future generations of computer chips according to Moore's law, without having to invest billions in new fabrication facilities (i.e. based on extreme ultra violet lithography) that may or may not be able to meet the resolution requirements already being demonstrated by DSA. For hard drives, block copolymer lithography is the only known technology to fabricate nanoimprint masters to manufacture bit patterned media at the required storage densities greater than 2 Tera dots/inch^2.

5.1 Design Goals

Directed Self-assembly of Block Copolymer Films for Lithography use-case group seeks to design block copolymer materials and assembly processes to enable manufacturing via DSA at length scales of 10 nm, scaling to 5 nm, and meet manufacturing constraints with respect to defects (0.01/cm^2), and line edge and width roughness (<1 nm). The structure of the assembled BCP depends on many variables describing material properties (molecular weight, block architecture, interaction parameter χ) and process parameters (temperature, solvent, assembly time, template chemistry and topography, interfacial

energies, and surface energies); our design objectives can only be met by developing and validating predicative multi-scale models. Moreover, the immense parameter space requires evolutionary approaches to simultaneously understand and optimize numerous variables, in the context of analysis of experimental data and in the design of new materials and processes. To accomplish our design goals with respect to structure, our priority and main activity is to advance three-dimensional metrology tools and methods, and develop expertise in quantitatively comparing predictive models and experimental data. The focus of former mentioned activities are the independent variables (design criteria) - material properties, template properties, and processing parameters. Molecular simulation-based data analysis is the foundation for delineating complex structure-property-processing relationships and is accomplished by close collaboration with Kline (NIST) and Sunday (NIST). As we recently reported, the dynamics of structure formation plays a dominant role in achieving our design goals with respect to minimizing number of defects in assembled structure. Our predicative models are being refined to include dynamic information, and new experimental tools based on high-speed AFM are used to quantify processing pathways.

5.2 Significant Accomplishments in 2015

A key roadblock to the design of materials and processes for sub 10 nm DSA, with scaling to 5 nm resolution is quantitative three-dimensional metrology, and relating structure to materials properties, template properties, and processing parameters. At these dimensions, main-stream metrology provides insufficient insight. A top priority of the user-case group, undertaken in partnership with NIST, is developing resonant soft x-ray scattering (RSoXS) as a technique to capture the details of the three-dimensional structure of individual block copolymer domains, and the collective averages of three-dimensional structure and pattern perfection over large areas, all as a function of materials, processing, and boundary conditions used in DSA. Because RSoXS requires BCP samples to be prepared on ultra-thin SiN membranes, in this funding period we devised sample preparation techniques for which all of the DSA processing on sub-10 nm high-χ BCP systems can be completed on the front side of the wafer prior to fabrication of the membrane by back etching. We also developed techniques to prepare samples cut from 300 mm wafers supplied by industrial partners to allow for analysis of the assemblies of highest value. To gain design-relevant information from the RSoXS experiments, we implemented a strategy to construct appropriate theoretically informed coarse grained (TICG) models during data analysis. Independent variables such as BCP molecular weight, composition, and interaction parameter χ, as well as template properties such as the chemistry and geometry of guide stripes and background regions are input into the model; simulations predict the three-dimensional structure which in turn is used to calculate RSoXS spectra. Evolutionary algorithms find the optimized combination of several independent variables input into the TICG model that results to the best comparison of the simulated and experimental data. Validation of the physics-based model and its use in the analysis of the RSoXS data, collected in reciprocal space, is obtained by transmission electron microscopy (TEM) tomography. TEM tomography enables direct visualization of a small area of the sample in real space. Based on the wealth of nanometer scale information in the RSoXS, and the extent to which this information is probed by our analysis method, we are optimistic that this MGI approach to predictive model development and validation is unprecedented in its power to guide the design of next generation DSA systems. Finally, in this funding

period we elucidated the relationship between the thermodynamics and kinetics of DSA processes and defects. Material and process parameters create a thermodynamic landscape, and kinetics determine if or for how long defects persist in metastable states at vanishingly small concentrations. Efforts are now underway to create new models to capture the dynamics and pathways of assembly, particularly nucleation of structure on the chemical guiding pattern. Simulation results will be contrasted to data from newly developed high speed AFM imaging of BCP films during processing.

5.3 Research Accomplishments

RSoXS of High χ Materials for Sub-10nm DSA. Over the Year Two funding period, we were able to reveal the complex 3D structures in block copolymer DSA, leveraging the expertise in nanofabrication and 3D characterization developed in the previous year. Through extensive collaboration with NIST and ANL, we combined both RSoXS and TEM tomography to investigate the materials and processes for the next generation sub-10 nm DSA. P2VP-b-PS-b-P2VP, a high χ system that can achieve sub-10 nm feature sizes, is an important candidate for Generation II DSA materials. P2VP-b-PS-b-P2VP triblock with 10.5 nm half-pitch was assembled using solvent vapor annealing on back-etched membranes. Samples with a different guide stripe width appeared aligned from top down views. However, RSoXS revealed complex 3D structures inside the film that were previously undetected. The results were confirmed by TEM tomography as presented in Figure 5.1. Characterizing and understanding these 3D structures is critical to identify the pattern geometries that would generate through-film domains for optimal pattern transfer.

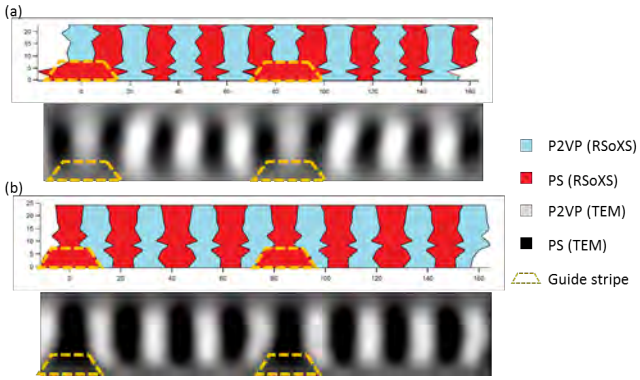


Figure 5.1: RSoXS and TEM average cross-sections characterization of P2VP-b-PS-b-P2VP DSA on different guide stripe widths: (a) 1.5 L_0 (b) 0.8 L_0. Stripe width of 1.5 L_0 led to a shorter P2VP domain on top of the guide stripe; at 0.8 L_0 PS appeared on top of the guide stripe while neighboring P2VP domains conformed to the sidewalls of the guide stripe and tapered at the bottom.

Material Design Based on Evolutionary Optimization. A key challenge for materials design is to identify the required components and their structural configuration for given target properties. In collaboration with the **de Pablo** group, the **Jaeger** group introduced a formalism that can generate optimizers automatically by extending statistical mechanics into the realm of design. The strength of this new approach lies in its capability to transform statistical models that describe materials into optimizers to tailor them. This formalism is broadly applicable, fast, and robust, and it provides a powerful tool for materials optimization as well as discovery. (see Figure 5.2)

X-ray Data Fitting Based on Molecular Model and Evolution Strategy. **Nealey** and **de Pablo** groups developed a synergistic methodology that links theory-based modeling to X-ray scattering data and vice versa. The overall scheme is illustrated in Figure 5.3. In

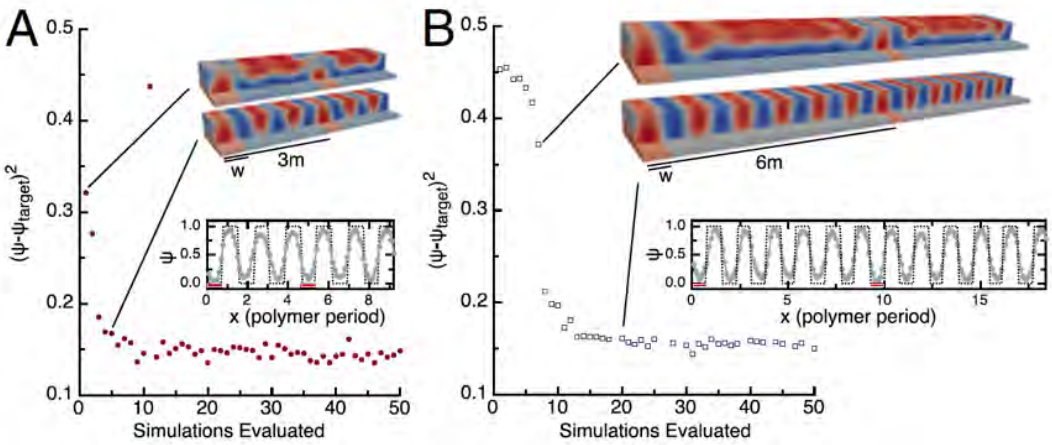


Figure 5.2: Pattern optimization for directed self-assembly. Optimized pattern parameters for 3x (A) and 6x (B) density multiplication, including guide stripe width and affinities of the guide and background regions, are obtained by matching the necessary BCP structure to the target morphology. Two characteristic configurations before and after optimization, separated by just a handful of iterations, display markedly different phases of the polymer. Asymptotic configurations depicting the order parameter (solid, marked line) and the target (dashed line) show that the optimized parameters match the desired morphology.

this work, experimental data drive an evolution strategy implemented on a finite number of modeling parameters. The latter then serve as input to molecular simulations that provide the necessary output. Tailored software then converts output to scattering predictions that are contrasted to experimental data and the procedure continues iteratively to achieve a satisfactory description of experimental data. The evolution strategy linked 3D data from scattering experiment directly to the fundamental modeling parameters. The latter can be then used for predictive modeling that develops new materials and processes by design.

3D Characterization of Industry-relevant Samples. DSA on chemical pattern using the "LiNe" flow developed by the **Nealey** group has been implemented on all-track process at Imec, a first in the industry. To transfer the 3D characterization techniques to the industry, we collaborated with Imec to adjust the back etch process and successfully prepared membrane samples from 300 mm wafers. By not damaging the crucial pattern-polymer interface, the back etch technique allowed the first experimental investigations of the 3D structures in samples from an industrial setting. This work was highlighted by the Semiconductor Research Corporation (SRC) as the Best in Patterning Session Award in TECHCON 2015. (see Figure 5.4)

Investigation of DSA kinetics with in-situ AFM. In the DSA process, the material and process parameters create a thermodynamic landscape, and kinetics determine pathways from the initial disordered state to the well-aligned structures. Monitoring the initial stages of microstructure nucleation therefore informs us of the processing conditions necessary to prevent the formation of metastable defects. It may be possible to reduce the number of defects formed at early stages of structure formation such that the kinetically slow processes of defect annihilation at late stages of processing become less important in terms of pattern perfection. *In situ* AFM uniquely allows the non-destructive, local monitoring of polymer dynamics, now achieving real-time video imaging with a rate of up to 1 image/second. In the preliminary analysis, we have observed the evolution of

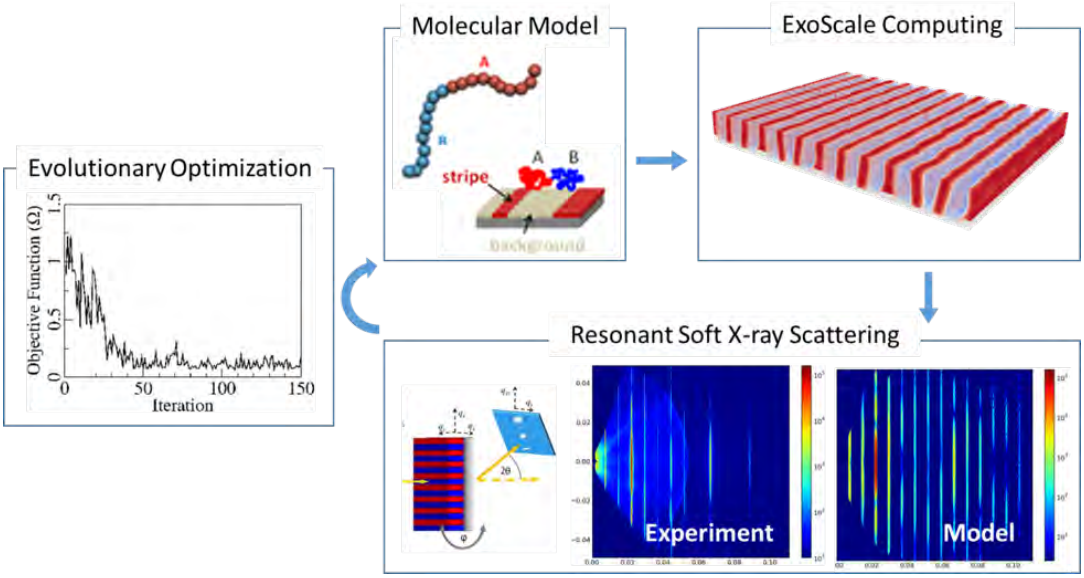


Figure 5.3: Overall scheme of scattering data fitting using evolution strategy. A finite number of modeling parameters serve as input to molecular simulations that provide the necessary structure. The real space structure is then converted to scattering predictions that are contrasted to experimental data and the procedure continues iteratively to achieve a satisfactory description of experimental data

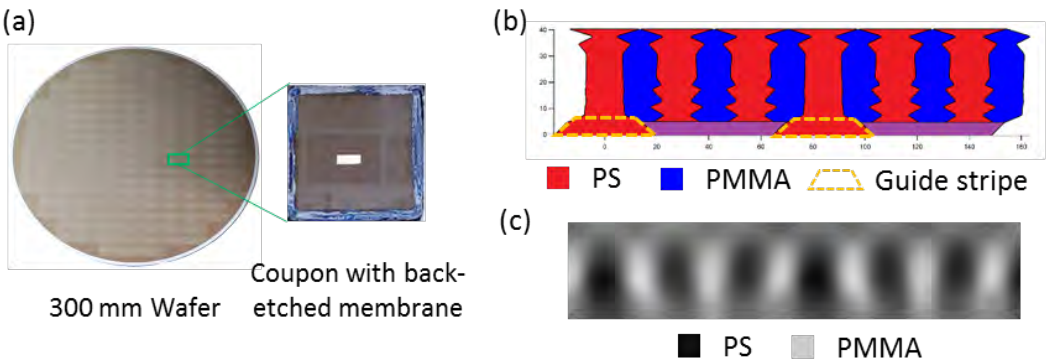


Figure 5.4: (a) Nealey group successfully prepared membrane samples from 300 mm wafer by back etching coupons. Average cross section of LiNe flow DSA was obtained by RSoXS (b) and TEM tomography (c).

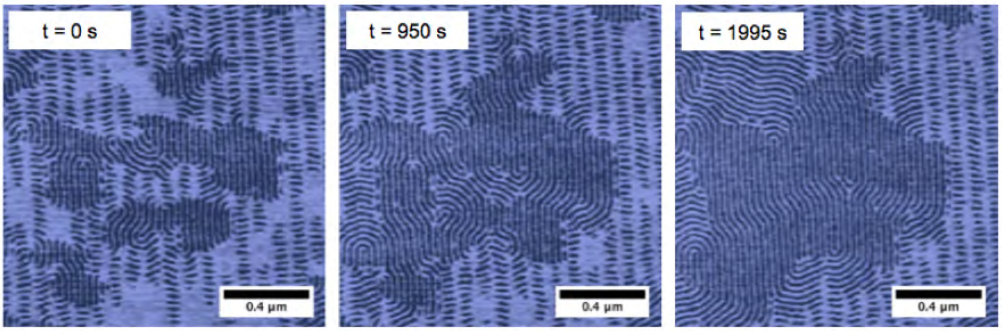


Figure 5.5: Growth and ordering of well-aligned lamellar domains on a chemically-patterned substrate at 240°C. The (vertical) well-aligned domains coexist with the (horizontal) non-bulk morphology.

well-aligned domains alongside non-bulk morphologies. As the film is thermally annealed, the lamellar domains were observed to grow and become more highly ordered. (see Figure 5.5)

Commissioning RSoXS beam line at the APS. Collaborating with Kline (NIST), CHiMaD funded post doc and student from the **Nealey** group performed first scattering experiment at the newly constructed Intermediate Energy X-ray (IEX) beam line, successfully testing the feasibility of carrying out RSoXS on polymer DSA at the IEX. *On the fly* RSoXS data analysis tools was also implement at the IEX beamline with the help of the Kline group (NIST). We aim to greatly improve the efficiency and quality of data collection. Great progress has also been made in the optimization of the beam line and testing is expected to finish in early 2016. (see Figure 5.6)

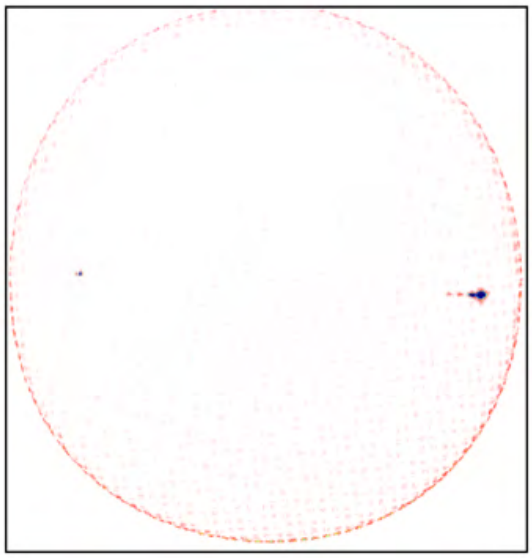


Figure 5.6: Specular (right) and 1st order (left) diffraction peaks taken on a patterned polymer sample infiltrated with aluminum oxide at the IEX beamline. The fact that both the specular reflection and the first order diffraction peak were visible proved that the detector has the required dynamic range for the study.

Polymer Property Data Base. Collaborating with Audus (NIST), **de Pablo** and **Foster** developed a semi-automated strategy for extraction of polymer properties from the recent literature. The first stage of this project focused on "chi" parameters for polymer blends, which are necessary for design of DSA processes. The contents of the data base were verified in course co-taught at the University of Chicago by Audus (NIST), Qin (UC), Tchoua (UC) and **de Pablo**. The data based now includes more entries for blend chi parameters than available literature compilations. A manuscript describing this semi-automated strategy was submitted for publication.

5.4 Collaborations

5.4.1 CHiMaD Collaborations

Materials Design for Dynamic Processes
*Juan **de Pablo** (UC), Heinrich **Jaeger** (UC)*
Through this collaboration a new evolutionary algorithm for materials design was developed. This algorithm is approximately two orders of magnitude more efficient (faster) than existing CMA (Covariance Matrix Algorithm) based strategies (also proposed by our group), and that can be used to identify dynamic processes leading to target properties in metastable, out-of-equilibrium systems. The results of that work have been published in the Proceedings of the National Academy of Sciences [3].

High-Speed AFM Imaging of Block Copolymer Microstructure Nucleation on Chemically Patterned Substrates
*Steven **Sibener** (UC), Paul **Nealey** (UC)*
The kinetics of initial BCP microstructure formation on patterned DSA substrates is critical to understanding the origin of metastable defects. High-speed AFM uniquely accesses these earliest stages, so we may better assess the processing conditions suitable for fabricating perfected films.

5.4.2 NIST Collaborations

Structure and Dynamics of Entagled Polymeric Nanocomposites
*Jack Douglas (NIST), Juan **de Pablo** (UC)*
Through this collaboration a new model for description of the structure and dynamics of entangled polymeric nanocomposites was developed. The model relies on a slip-spring formalism to capture entanglement effects on the linear and non-linear rheology of such systems. A manuscript is being prepared for submission for publication.

Structure of Thin Polymer Films
*Jack Douglas (NIST), Steven **Sibener** (UC)*
Douglas and Sibener groups have interacted on graphoepitaxy, dynamics of polymer structural evolution, and the effect of additives such as nanoparticles on local structure in thin polymer films.

Physics Based Interpretation of Scattering Data
*Joseph Kline (NIST), Daniel Sunday (NIST), Paul **Nealey**, Juan **de Pablo** (UC)*
Through this collaboration a new formalism that enables interpretation of 3D scattering data for directed self-assembly of block polymers by relying on a physics-based model of the material is being developed. The formalism relies on evolutionary strategies to describe the experimental data, and it is the first of its kind, raising exciting prospects for development of a new generation of metrology tools. Two manuscripts are being prepared for submission for publication.

TEM Tomography of Block Copolymers
*Jonathan Winterstein (NIST), Alexander Liddel (NIST), Paul **Nealey** (UC), Juan **de Pablo** (UC)*
This use-case group collaborated with Dr. Winterstein (NIST) and Dr. Liddel (NIST) to develop the TEM tomography techniques for 3D visualization of the block copolymer structures.

Advanced RSoXS Data Analysis Techniques
*Adam Hannon (NIST), Paul **Nealey** (UC), Juan **De Pablo** (UC)*
Members of the CHiMaD team and the NIST team are actively collaborating in advanced RSoXS data analysis techniques based on molecular simulations. To this end Adam Hannon (NIST) spent more than six weeks in Chicago working with the **de Pablo** group.

Polymer Property Data Base *Debra Audus (NIST), Jack Douglas (NIST), Ian Foster (UC), Juan de Pablo (UC), Ken Kroenlein (NIST)*
Members of CHiMaD and NIST collaborate on development of automated tools for data extraction from the literature and creation of a data base of polymer properties for design of DSA processes. Audus (NIST) spent a month at the University of Chicago participating in this collaboration and developing a course on data base creation. As part of this collaboration, a polymer property predictor tool was developed that includes models for homopolymers, copolymers, and charged polymers. Tchoua (UC) visited Kroenlein (NIST) at Boulder to discuss their efforts to extract literature data in the context of thermodynamic fluid properties for process design.

5.5 Technology Transfer

Software
3D Block Copolymer Simulator
J. de Pablo, P. Nealey, P. Theofanis (INTEL)
Through this collaboration user-friendly versions of the 3D block copolymer simulators were developed and transferred to the industry. This simulation package is now being used in a commercial setting at INTEL for development of new DSA materials and processes.

Software
Polymer Property Data Base
D.Audus (NIST), I. Foster (UC), J. de Pablo (UC), R. Tchoua (UC)
Link to beta distribution: http://pppdb.uchicago.edu/ The first stage of this project is focused on "chi" parameters for polymer blends, which are necessary for design of DSA processes. The data based now includes more entries for blend chi parameters than available literature compilations.

Technology
"LiNe" Flow Directed Self-Assembly Method
P. Nealey, R. Gronheid (imec)
DSA on chemical pattern using the "LiNe" flow developed by the **Nealey** group has been implemented on all-track process at IMEC, a first in the industry. To transfer the 3D characterization techniques to the industry, we collaborated with IMEC to adjust the back etch process and successfully prepared membrane samples from 300 mm wafers. Please see section 5.3 for more information.

Technology and Know-How
Short-Course on DSA
P. Nealey, J. de Pablo and R. Gronheid A short course on DSA to participants from industry was taught at the SPIE meeting in San Jose, California, in February 2016. The course was attended by practicing scientists and engineers from many of the major semiconductor companies involved in DSA.

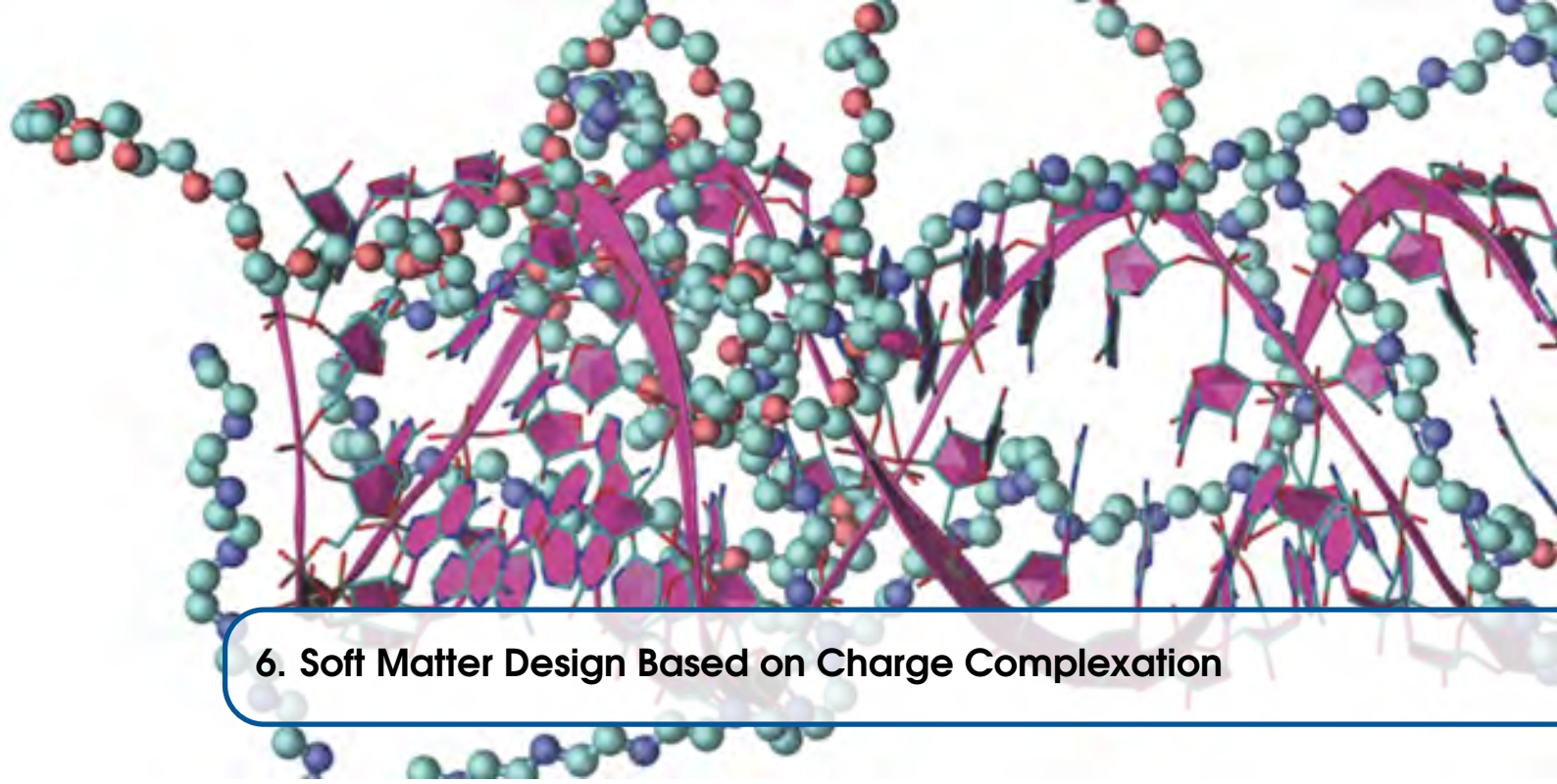
5.6 Publications and Presentations

6 Number of CHiMaD-supported publications in 2015 by Directed Self-assembly of Block Copolymer Films for Lithography use-case group. Please see chapter 20 for details. [3, 4, 5, 6, 7, 8]

15 Number of presentations on CHiMaD supported research in 2015, please see section 21.5 for the complete list.

5.7 CHiMaD Team

DSA of Block Copolymers for Lithographic Applications Use-Case Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Paul Nealey	Principal Investigator	UC/IME	
Juan de Pablo	Principal Investigator	UC/IME	
Steven Sibener	Principal Investigator	UC/CHM	
Luping Yu	Principal Investigator	UC/CHM	
Heinrich Jaeger	Principal Investigator	UC/PHY	
Kieran Murphy	Graduate Student	UC/PHY	*(Jaeger)*
Gurdaman Khaira	Graduate Student	UC/IME	Evolutionary algorithms for materials design of DSA *(de Pablo/Nealey)*
Brandon Peters	Graduate Student	UC/IME	Directed Self-Assembly of Block Copolymers *(de Pablo)*
Alec Bowen	Graduate Student	UC/IME	Directed Self-Assembly of Block Copolymers *(Nealey)*
Roselyne Tchoua	Graduate Student	UC/IME	Creation of chi-parameter Database *(Foster)*
Jian Qin	Graduate Student	UC/IME	*(de Pablo)*
Jonathan Raybin	Graduate Student	UC/CHM	Directed Self-Assembly of Block Copolymer Films for Lithographic Applications *(Sibener)*
Katherine Oosterbaan	Undergraduate Student	UC/CHM	Directed Self-Assembly of Block Copolymer Films for Lithographic Applications *(Sibener)*
Tim Csernica	Undergraduate Student	UC/CHM	Directed Self-Assembly of Block Copolymer Films for Lithographic Applications *(Sibener)*



6. Soft Matter Design Based on Charge Complexation

Matthew Tirrell (UC), Juan de Pablo (UC), Erik Luijten (NU), Monica Olvera de la Cruz (NU)

Significance

Soft matter refers to materials where energies of order kT can influence the structure and functions of the materials. One of the main inspirations for soft matter design comes from biology, where many functional materials are built from relatively weak non-covalent interactions. Considerable success has been achieved in creating new materials based on hydrogen bonding and van der Waals interactions. In addition these bonding modalities, and others, biology makes extensive use of electrostatic interactions, frequently mediated by multi-valent ions, including charged polymers. The Use-Case on Soft Matter Design based on Charge Complexation is a comprehensive effort to understand, and employ this understanding to design, new materials based on predictive use of attractive interactions induced by multi-valent interactions in systems of charged polymers. This Use-Case comprises experimental and theoretical work measuring, simulating and modeling phase diagrams in charged polymer systems, micellization and hydrogel formation in charged block copolymers, and organic inorganic nanocomposites. New materials are being designed and synthesized for biomaterials, drug and gene delivery, bone and tooth repair.

6.1 Design Goals

The overall design goal of the Soft Matter Design Based on Charge Complexation is to arrive at functional, self-assembled systems for applications in health care. Examples include micellar nanoparticles, which may be used for controlled drug delivery, bio-imaging, or gene delivery. In that case the design goal is to develop self-assembled complexes having a specific size, structure and charge, as well as clearly defined characteristic thermodynamic properties. Examples also include calcium phosphate nanoparticles, formed by charge complexation, which may be used for bone replacement therapy or dental repair. In this case the rheological and mechanical properties of the material are of central importance to the end use, as well as their compatibility with bone cells. This field is in its infancy, and in

order to meet these design goals it is necessary to generate the necessary thermodynamic and rheological data on model systems, it is necessary to develop models capable of describing such data, and it is necessary to develop prototypes, consisting of self-assembled materials, with which to test some of the central design principles identified and developed by the use case.

Quantitative Data on Phase Behavior of Complexes Formed by Charged Homopolymer and Block Copolymers. **Tirrell** group aims to develop quantitative data on phase behavior of complexes formed by charged homopolymer and block copolymers. This information is essential to knowing the properties of the materials formed by complexation such as viscosity and modulus, which are directly related to phase data such as water content.

Quantitative Prediction of Phase Diagrams in Multi-valent Polyelectrolyte Systems. **Olvera de la Cruz group** is developing a self-consistent field approach to the quantitative prediction of phase diagrams in multi-valent polyelectrolyte systems. This work is especially important in capturing the effects of ion correlations on the phase behavior of polyelectrolyte blends.

De Pablo developed a multi-scale modeling formalism for prediction of the phase behavior and rheology of coacervates. This work is crucial for understanding the dynamic properties of charged polymers, including complex coacervates.

Dielectric Effects in Self-assembly. **Luijten** group has developed a new method for taking into account dielectric effects in self-assembly, which is being applied to the design of complexes between synthetic polymers and nucleic acids for the purposes of manipulating gene expression.

New System Development. **De Pablo** and **Tirrell** and co-workers have developed a system composed of a complex between a synthetic polyelectrolyte and CaP that produces a paste with useful tunable properties the optimal design of which are currently under investigation.
Data Base and Property Prediction Software **De Pablo**, in collaboration with Douglas (NIST) and Audus (NIST), developed a polymer property predictor software that couples to a polymer property data base and permits calculation of phase diagrams, including for charged polymers (and coacervates).

New Force Field Development **De Pablo** group has developed a new atomistic force field for simulation of calcium phosphate in aqueous solution. The model is being used to describe the formation of amorphous calcium phosphate nanoparticles.

6.2 Significant Accomplishments in 2015

Towards Predictive Design of Complex-based Materials. **Tirrell** group have determined the water content in a series of complex coacervate phases formed from different initial solution concentrations ranging from 1 to 30%. To very good accuracy, all formed complex phases with 60% water content, and all exhibited equi- partitioning of salt between supernatant and condensed phases. If this result hold up to further experimental scrutiny, it will greatly simplify predictive design of complex-based materials.

Phase Diagrams of Charged Block Copolymers. **Tirrell** group, in collaboration with Prabhu (NIST) have expanded our knowledge of the phase diagrams of charged block copolymers by synthesis and scattering (x-ray and neutron) studies of multiple new block copolymer samples. Matched sets of di-block and tri-block copolymers behave differently

(Figure 6.1). We have shown that while oppositely charged diblock copolyelectrolytes assemble into micellar assemblies as expected, their triblock analogs prefer to form interconnected networks and segregate from the bulk of the solution. Next section provides further explanation.

Coarse-Grained Modeling Tool for Complex Coacervation. **De Pablo** group has developed an extended version of its "Theoretically Informed Coarse Grained (TICG)" model for polymer simulations capable of describing the properties of charged polymers. The tool is important in that it is built on the same principles as the tools developed for polymer nano-composites and for DSA, thereby providing a unifying framework with which to simulate and engineer wide classes of polymer materials. Importantly, this tool can also be used to predict rheological properties.

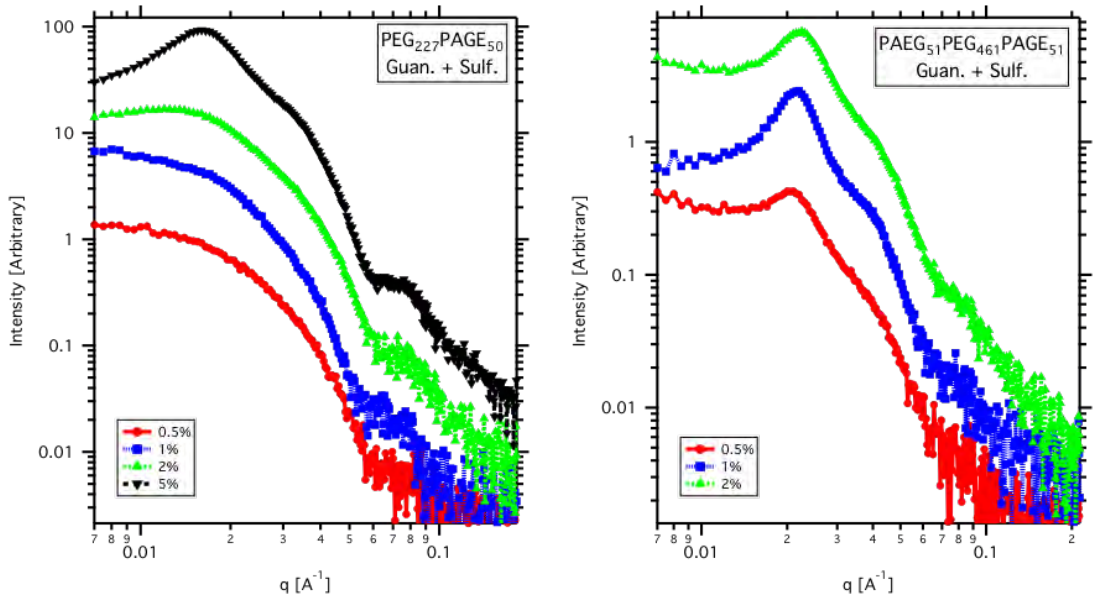


Figure 6.1: Scattering intensities from poly (allyl glycidyl ether-b-ethylene glycol) based (A) diblock and (B) triblock copolyelectrolytes based assemblies at varying total polymer concentrations in solution. The scattering curves are shifted for the clarity of presentation.

Phase separation in polyelectrolyte blends. **Olvera de la Cruz** group has identified two driving forces for phase separation in polyelectrolyte blends: ionic correlations, described by Γ (in kT), between the charged backbone and counterions, and Flory-Huggins interactions, described by χ N. Ionic correlations play a particularly important role in blends with a low concentration of charges, while Flory-Huggins interactions drive phase separation in blends with high charge concentration. In charge-dilute blends, phase separation can be driven entirely by ionic correlations to form ionic clusters and pairs.

Analytical generalization of image charges. **Luijten** group's simulation approach provides the first analytical generalization of image charges in decades, extending it to arbitrary multipoles. By combining this discovery with expansions based upon spherical harmonics, we developed a method that provides the energies and forces between dielectric objects. Our method scales linearly with the number of dielectric objects in a system and accelerates calculations by at least three orders of magnitude compared to the most advanced existing methods. This opens the way to large-scale scanning of parameter space to explore the role of dielectric effects.

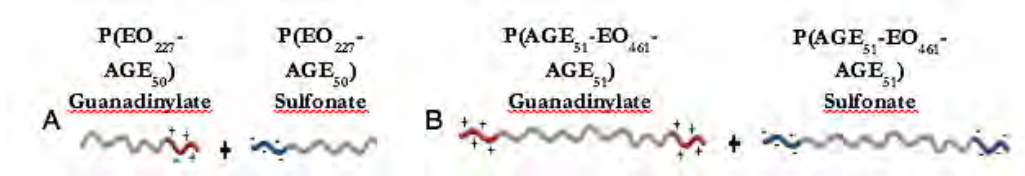


Figure 6.2: Representative poly (allyl glycidyl ether-b-ethylene glycol) based A. diblock and B. triblock copolyelectrolytes.

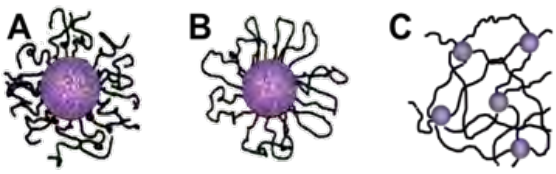


Figure 6.3: Diverse PEC based self-assembled structures. (A) Hairy micelles, (B) flower like micelles and (C) Interconnected PEC aggregates. The water content of the complex domains is a key issue. Schematic not to scale.

Synthesis of oppositely charged amorphous nanocomposite nanoparticles. Collaborative efforts of the **de Pablo** and **Tirrell** groups have been able to prepare oppositely charged amorphous nanocomposite nanoparticles consisting of amorphous calcium phosphate nanospheres and an organic polymer. Importantly, we have demonstrated that upon mixing of these nanoparticles, it is possible to produce injectable pastes with controlled properties for potential applications in bone and teeth repair.

6.3 Research Accomplishments

Oppositely charged polyelectrolyte block copolymers in aqueous solution. Assemblies of oppositely charged polyelectrolyte block copolymers in aqueous solutions at low polymer concentrations have been studied in detail. Oppositely charged polyions complex with each other, and in process phase separate from the bulk solution. In mixtures of A_+B and A_-B diblock copolymers (A_+ and A_- being the charged blocks, B being the neutral block, (Figure 6.2A)), however, the neutral block preferentially stays in the bulsolusolution, leading to micellar assemblies with a polyelectrolyte complex (PEC) cores, the neutral block forming the corona, and the diblock junction points residing on the core-corona interface (Figure 6.3A). Scattering from such an assembly would constitute contributions from the individual micelle scattering (form factor) and from the inter-micelle correlations (structure factor), with only the latter being dependent on the number concentration of the micelles. Small angle X-ray scattering (SAXS) measurements on $P(EO_{227}{-}AGE_{50})$ based diblock copolyelectrolyte micelles show a progressively increasing correlation peak with increasing polymer concentration concomitant with increasing contribution from the inter-micelle correlations. At low concentrations (0.5 and 1 wt% total polymer concentration in solution), the scattering intensity represents the micelles form factor, as is evident from (Figure 6.3A) for (shown in red and blue curves, respectively). At higher concentration, the inter-micelle correlations contribute notably to the scattering intensity, and lead to the appearance of a structure factor peak in 2 wt% and 5 wt% total polymer concentrations in solution at 0.017 $Å^{-1}$ and 0.0235 $Å^{-1}$, respectively (blue and black curves in Figure 6.1A). The inter-micelle distance can roughly be estimated from the structure factor peak position (d $2\pi/q_max$), and for the 2 wt% and 5 wt% solutions corresponds to 370 Å and 270 Å, respectively.

Nanocomposite nanoparticles for bone and dental repair. **Tirrell** and **de Pablo** groups have produced a new paste material with significant possibilities for applications in bone and dental repair. The building blocks of the paste, i.e. the hybrid nanoparticles of controlled size and stability, form spontaneously through a simple process under mild conditions. We have also found that the characteristic dimensions of the as-synthesized polymer/amorphous CaP (ACaP) hybrid nanoparticles can be controlled by polymer molecular weight, as well as the concentration of the polymer and salts in the environment. Note that a wide array of complementary characterization techniques has been used to characterize their shape and internal structure. Dynamic light scattering (DLS) was used to monitor size stability of the nanoparticles and to provide direct evidence for the ability of the oppositely charged hybrid nanoparticles to self-assemble into cohesive aggregates upon mixing. Elastic, shear-thinning pastes of tunable elastic modulus were formed by relying on the electrostatically driven self-assembly of oppositely charged hybrid nanoparticles of different sizes. The pastes have been engineered to be continuously injected through medical syringes equipped with needles of different sizes, and can preserve their structure after injection into an aqueous media. Taken together, these properties render our designer pastes a simple, inexpensive material that could be applied in minimally invasive bone repairing surgeries that require injectable formulations.

Melt phase behavior of polyelectrolyte blends. **Olvera de la Cruz** group has investigated the melt phase behavior of polyelectrolyte blends with and without salt. Polyelectrolyte blends, where one species is charged and the other neutral, can serve as a model system for a mixture of oppositely charged polyelectrolyte chains, which form polyelectrolyte complexes (PECs). We have identified two driving forces for phase separation in polyelectrolyte blends: ionic correlations, described by Γ (in kT), between the charged backbone and counterions, and Flory-Huggins interactions, described by χ N. Ionic correlations play a particularly important role in blends with a low concentration of charges, while Flory-Huggins interactions drive phase separation in blends with high charge concentration. In charge-dilute blends, phase separation can be driven entirely by ionic correlations to form ionic clusters and pairs. By a careful selection of Γ and χN values, we can observe a triple point (Figure 6.4), where the three coexisting phases differ in ionic structure and ion concentration. From the radial distribution functions shown in Figure 6.5, it is estimated that the ions are ordered in a liquid-like fashion in ion-dense phase, form small clusters in ion-intermediate phase, and form pairs in ion-dilute phase. The addition of salt to the polyelectrolyte blend can induce re-entrant behavior as the salt concentration is increased.

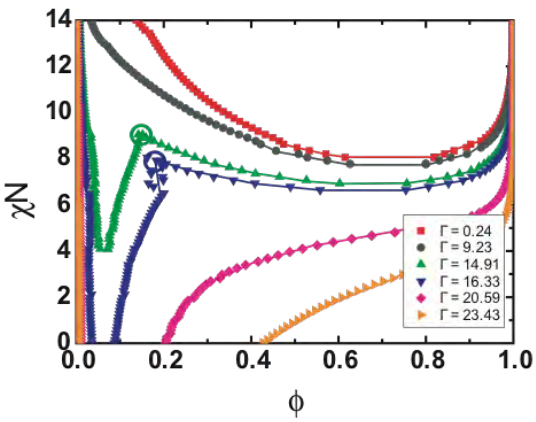


Figure 6.4: Effect of Γ on the phase diagram of symmetric polyelectrolyte blends with N = 40, and charge fraction of 0.2. Hollow circles indicate the triple point

Melt phase behavior of polyelectrolyte blends. We have extended the scope of charged block copolymer phase diagrams via the introduction of several new copolymer samples synthesized during Year Two. As seen in Figure 6.6 below, increasing the length of the

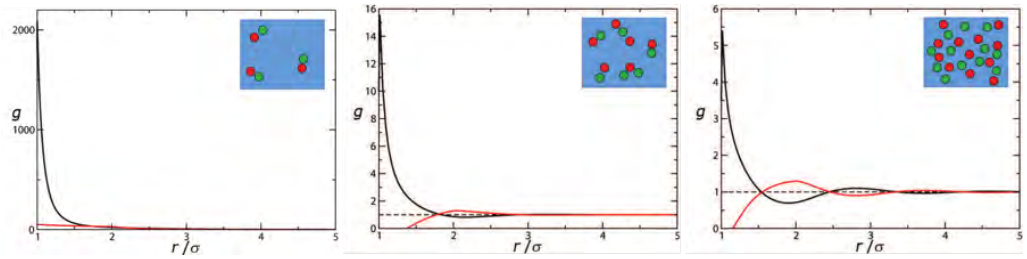


Figure 6.5: Radial distribution functions of the ions of coexisting phases close to the triple point. The insets show cartoons of the estimated morphologies. The strong peak of the g(r) of the dilute phase hints at pair formation. The second oscillation at the intermediate density hints at a significant fraction of triplets and larger clusters. The oscillations in the g(r) of the dense phase are caused by a liquid-like ordering of charges

charged end block in tri-block systems such as those in Schematic 6.2B, leads to the formation of lamellar phases while reducing the endblock length destabilizes ordered phase formation leading only to disordered suspensions of micelles.

6.4 Collaborations

6.4.1 NIST Collaborations

Coarse-grained Model for Simulation of the Phase Behavior of Polyelectrolytes
*Jack Douglas (NIST), Juan **de Pablo** (UC), Matthew **Tirrell** (UC)*
Through this collaboration a coarse-grained model for simulation of the phase behavior of polyelectrolytes was developed that includes an explicit description of solvent and ions. The model is the first to be able to describe complex coacervation in polymeric systems. A manuscript is being prepared for submission for publication.

Semi-automated Data Base Creation
*Debra Audus (NIST), Ian **Foster**, Juan **de Pablo** (UC), Matthew **Tirrell** (UC)*
Through this collaboration, we have developed a model for semi-automated data base creation. The current process now involves a verification step, which was implemented by teaching an undergraduate course at the University of Chicago during which students were asked to check the relevance of automated data entries into the data base. Dr. Audus (NIST) spent three weeks at Chicago collaborating on this project and co-teaching that course. A manuscript describing this project has been submitted for publication in the Journal of Chemical Education.

6.4.2 External Collaborations

Hybrid methods for dielectric materials
*Erik **Luijten** (NU), Zhenli Xu (Shanghai Jiao Tong University, China), Shidong Jiang (New Jersey Institute of Technology)*
Prof. Xu and Prof. Jiang are experts on highly efficient boundary integral methods and dielectric methods. This collaboration aims to combine their innovative ideas with the **Luijten** groups new strategies for dealing with dielectric interfaces.

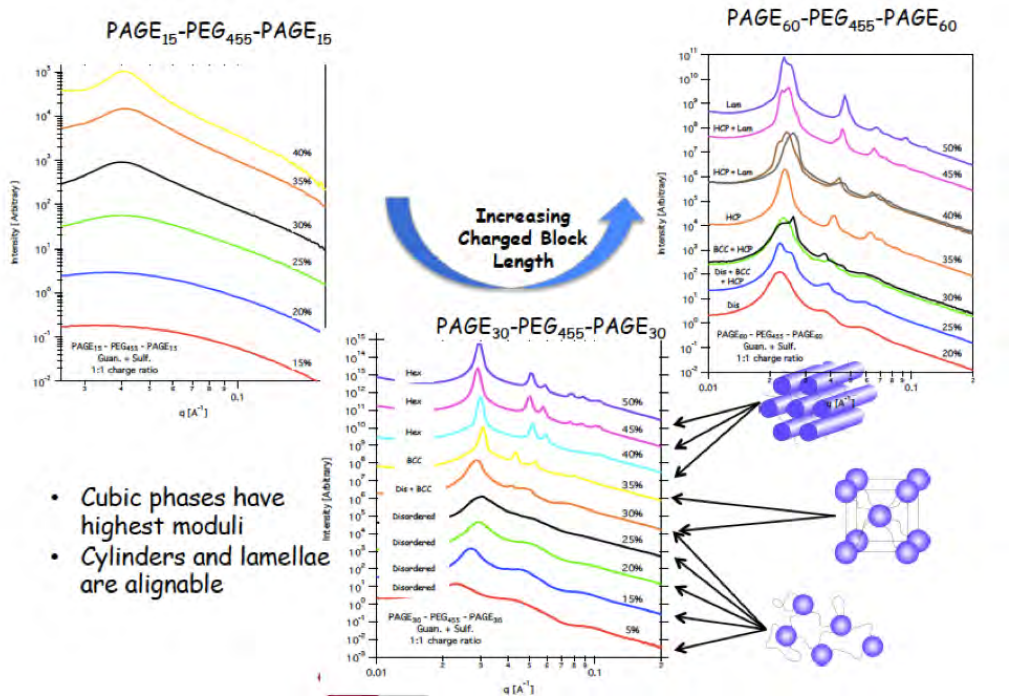


Figure 6.6: Increasing end block length drives system into lamellar phases, while reducing endblock length destabilizes self-assembled ordered phases.

6.5 Publications and Presentations

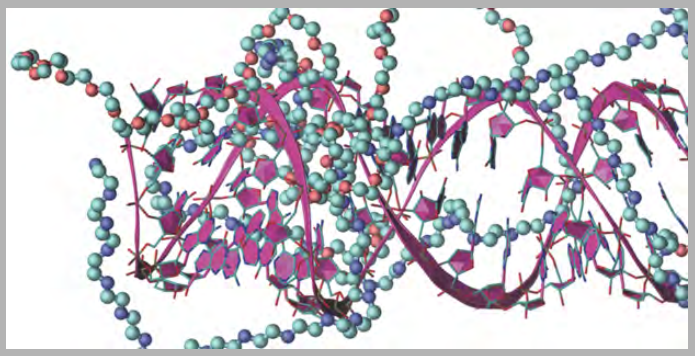
6 Number of CHiMaD-supported publications in 2015 by Soft Matter Design Based on Charge Complexation use-case group. Please see chapter 20 for details. [3, 6, 7, 8, 9, 10]

28 Number of presentations on CHiMaD supported research in 2015, please see section 21.4 for the complete list.

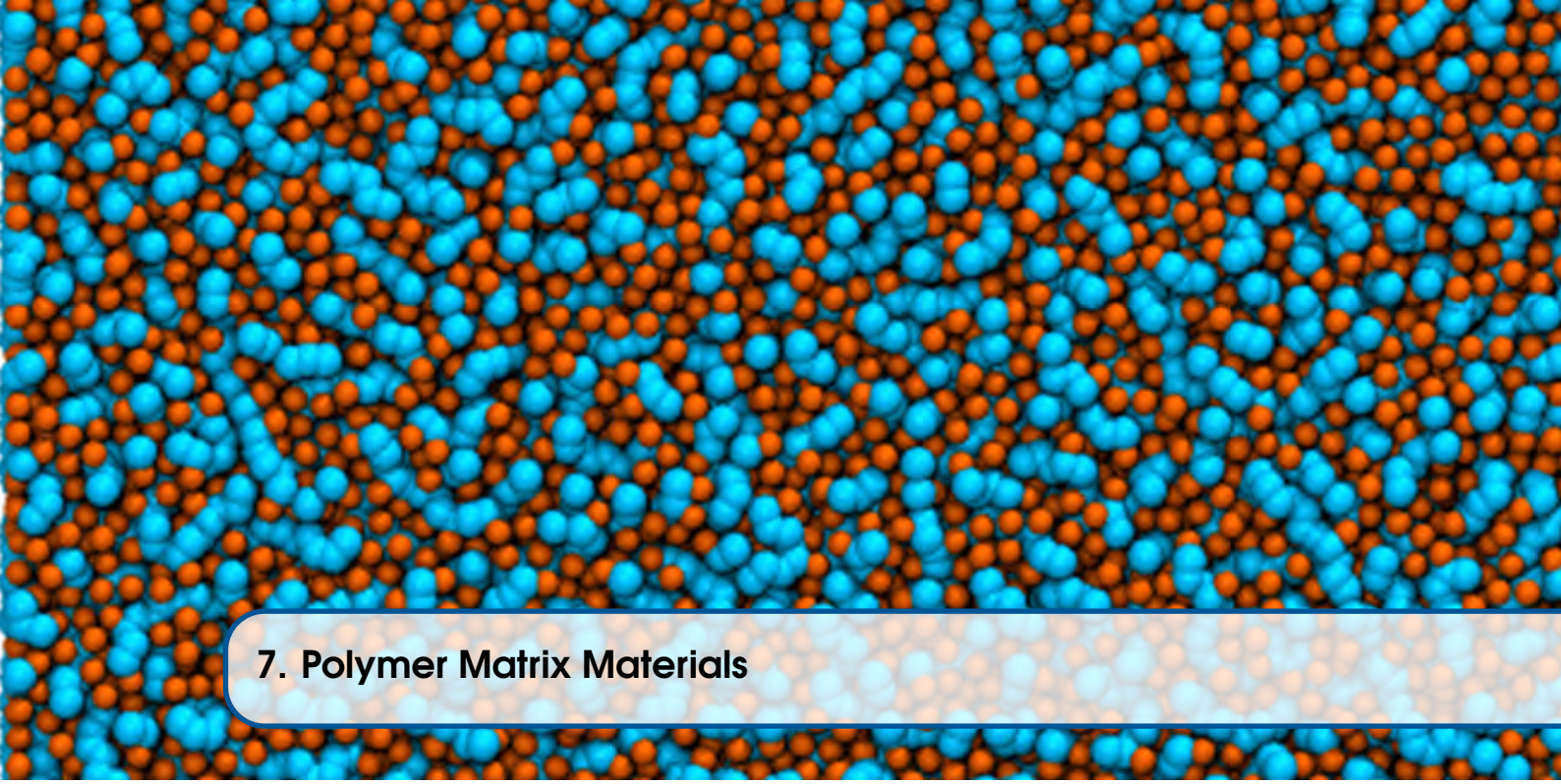
1 Soft Matter Design Based on Charge Complexation use-case group organized an international symposium entitled *Multivalent Interactions in Polyelectrolytes: New Physics, Biology and Materials* held at Institute of Molecular Engineering, University of Chicago on October 2-4, 2015.

6.6 CHiMaD Team

Soft Matter Based on Charge Complexation Use-Case Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Matthew Tirrell Juan de Pablo Erik Luijten Monica Olvera de la Cruz	Principal Investigator Principal Investigator Principal Investigator Principal Investigator	UC/IME UC/IME NU/MSE NU/MSE	
Samanvaya Srivastava	Postdoctoral Researcher	UC/IME	Predictive design of complex-based materials *(Tirrell)*
Nader Taheri Qazvini	Postdoctoral Researcher	UC/IME	Hybrid biomaterials *(de Pablo/Tirrell)*
Marat Andreev	Postdoctoral Researcher	UC/IME	Biomaterials *(de Pablo)*
Ashley Guo	Graduate Student	UC/IME	Biomolecule aggregation and detection *(de Pablo)*
Jiyuan Li	Graduate Student	UC/IME	Biomaterials *(de Pablo)*
Hadi Ramezani-Dakhel	Graduate Student	UC/IME	Biomaterials *(de Pablo)*
Ha-Kyung Kwon	Graduate Student	NU/MSE	Biomaterials *(Olvera de la Cruz)*
Ming Han	Graduate Student	NU/AP	Dielectric Interfaces *(Luijten)*
Zonghui Wei	Graduate Student	NU/AP	Coarse-grained models for PEI *(Luijten)*
Huanxin Wu	Graduate Student	NU/AP	Computational methods for spatially varying permittivity *(Luijten)*
Jos Zwanikken	Assistant Professor	UM/PHY	Biomaterials *(Olvera de la Cruz - partial funding)*



Header Image: Complexation of PEI-PEG graft copolymer with RNA, demonstrating how the double helical structure contracts in the binding process. Models developed within the CHiMaD use-case provide quantitative predictive capabilities that greatly accelerate the design process of polymeric carriers for DNA and RNA nanoparticles (Luijten, from Publication [10]).



7. Polymer Matrix Materials

Catherine Brinson (NU), Wei Chen (NU), Juan de Pablo (UC), Sinan Keten (NU), Erik Luijten (NU)

Significance

While polymer composites are lightweight, corrosion resistant and with tailorable properties, their capabilities are vastly under-utilized due to lack of: 1) understanding of multiphase composite properties under small constituent changes, 2) ability to tailor multiple physical properties simultaneously, and 3) durability predictions for long-term properties under use conditions. Tackling these challenges requires a fundamental understanding of the nature of polymer behavior near interfaces (the interphase) and ability to predict microstructure and its impact on properties. In this use case group, we pursue an integrated approach to to relate macroscale polymer composite behavior to chemical constituent and kinetic behavior, and link these resources to development of high-performance modeling and predictive tools. The research includes experimental investigations mapping local physical properties, simulations and analysis to predict microstructure and interphase formation, and a data analytics approach to curate, visualize, and develop analysis and design tools.

The focus of the Polymer Matrix Materials use-case group is initially on polymer nanocomposites, with a long term vision for traditional and hybrid composites. The key of multiphase polymer response is to understand the interaction of filler particles with the matrix material and to explore the physical properties of the interphase zone. This is accomplished both by experimental efforts and physics-based modeling using Molecular Dynamics (MD) and Monte Carlo (MC) simulations to predict interphase polymer response as a function of confinement, crosslinking density and monomer chemistry. At the same time, the researchers of the Polymer Matrix Materials use-case are assembling the known data into a central resource, which will be used with supervised learning methods to identify overarching trends. Combining the physics based methodology with the curated data and tools will provide an unprecedented ability to develop new predictive models of composite behavior.

7.1 Design Goals

The ultimate goal for the Polymer Matrix Materials use-case is to develop databases, models and tools to enable prediction of hierarchical composite behavior based on constituent components and processing.

In short term this use-case aims to;

- Develop the fundamental understanding of interphase properties in cellulose-polymer nanocomposites
- Develop databases, models, and tools to manipulate and design interphase properties in cellulose-polymer nanocomposites and thus control their bulk physical properties (e.g. diffusion, modulus, T_g)
- Develop design rules to tune properties and control service life (e.g., double interphase modulus and double freeze-thaw cycles)

7.2 Significant Accomplishments in 2015

The polymer matrix materials use case has integrated modeling and experimental work to understand the origins of the interphase in polymer-particle systems, curated data on structure and properties, and developed analysis and design tools for nanocomposite systems. Fundamental research on the interphase has produced local property gradients for polymers near cellulose surfaces both experimentally and in simulation. The results show the impact of molecular weight, entanglement and surface chemistry, where significant new modeling approaches have been validated with significantly improved computational speed. A data resource has been built, *NanoMine*, curating data on polymer nanocomposites from literature and our own data utilizing schemas developed for the *Materials Data Curator* system at NIST. Microstructure characterization analysis and characterization tools have been developed and included in *NanoMine*. These tools allow reduction of microstructural images to numerical descriptors and computational reconstruction of statistically equivalent images in 2 or 3 dimensions which can be used in further simulation and design simulations. In one application of the data resource, the processing energy and surface energies for a suite of different polymer-particle systems was analyzed and a model developed to relate these energies directly to property descriptors. It was shown that final dispersion is more strongly related to the interfacial energies than the processing energies. The accomplishments represent both fundamental new understanding in polymer physics, development of new open-source data and tool resources, and the foundation for true materials design in this complex arena.

7.3 Research Accomplishments

Data Structures and Databases for Polymers and Composites Polymer composites and nanocomposites (PNCs) present the distinct challenge of being a system of organic polymer or matrix coupled often times with an inorganic reinforcing filler phase, rendering such material systems impossible to be thermodynamically simulated from first principle calculations. A point of emphasis in this project has therefore been to create a centralized repository of PNC data from many different sources, including published literature, and a range of data analysis tools that enable quick and efficient mining of the data within the repository, thus aiding the effective identification of hitherto unknown parameters that control the structure-property relationships in PNCs and enhance the pace of material

discovery. Such an open-source, centralized data resource, which can be easily accessed by the research community, is envisioned to encourage collaborative contribution of data and data-analysis tools developed by different researchers, replacing the currently tedious and inefficient manual data collection, comparison and analysis efforts performed within individual research groups. This objective was achieved through the development of a novel data resource for PNCs called *NanoMine* (**Brinson, Chen**, Zhao (NU)) through customization of the *Materials Data Curator* (MDC) system developed at NIST with suitable data structures for experimental and computational PNC data.

The development of *NanoMine* database involves three distinct tasks: (i) creation of suitable templates and material data structures ("schemas'") for PNCs, (ii) population/curation of the database with representative sets of PNC data, and (iii) development and integration of data-analytics tools and physics-based modeling tools (**Brinson, Chen**, Li (NU)). Detailed templates and hierarchical schemas capable of archiving important processing, structure and property attributes in PNCs have been developed and are being updated on the basis of an ongoing data curation process. The initial curation efforts, which also contributed to enabling undergraduate summer outreach (Qu (NU), Schmutz (NU)), were primarily focused on curating published data from PNCs with surface treated spherical inorganic nanofillers with explicit reports of nanophase dispersion in micrographs, well-documented processing and experimental procedure, and functional data of viscoelastic and/or dielectric properties. More than 500 data sets from experiments and nanocomposite literature have been manually curated and entered into *NanoMine*.

Modular statistical learning tools for characterizing material microstructure have also been developed and integrated with the *NanoMine* database. The *Niblack Binarization* module enables the characterization of the material microstructure from SEM/TEM images, wherein the individual pixels are assumed to contain background information that is influenced by and correlated to the neighboring pixels. This approach results in flexible and enhanced binarization of microstructural features by allowing the user to tune the size of the pixel neighborhood. Similarly, a descriptor-based three dimensional reconstruction from a two dimensional image can be achieved using the *Descriptor Characterization* module. A third module, *Dynamfit*, that is currently being integrated into *NanoMine* will enable the users to fit a Prony series to viscoelastic master curves, and use the output functional responses in Finite Element Analysis (FEA) simulations of viscoelastic properties.

A descriptor-based approach, with two energy descriptors, i.e., processing energy and interface energy has also been developed to study the processing-structure relationship of polymer nanocomposites (**Brinson, Chen**). Supervised learning approaches were applied on microstructure images, wherein these two processing descriptors were correlated with the key microstructural descriptor, normalized interface area. The learned processing-structure correlation has been validated on polymer nanocomposites with different combinations of constituents and surface modification methods, which will aid the ongoing experimental (**Brinson**, Fox (NIST), Gilman (NIST)) and computational (**Keten, Luijten**) efforts aimed at understanding the effects of changes in surface energy (arising from controlled changes in surface functionalization) of Cellulose Nano Crystal (CNC) filler particles on the functional properties of PNCs. The complementary *Polymerizer* simulation module (**Brinson, Chen**), developed in collaboration with research groups at Rensselaer Polytechnic Institute (RPI), has been integrated into *NanoMine* to enable users to predict surface energy parameters in nanocomposites, including work of adhesion, wetting angles

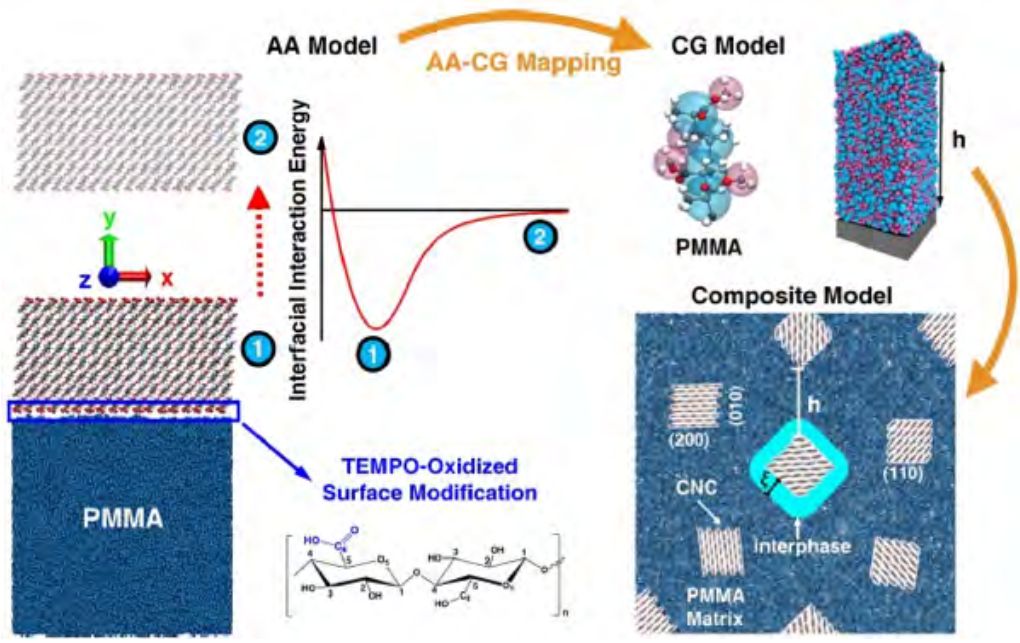


Figure 7.1: The results of the all atomistic molecular dynamic simulations have been used in coarse-grained MD (CG-MD) simulations of model nanocomposite systems to capture the local changes in glass transition temperatures (T_g) of the interphase regions.

and work of spreading using curated particle surface energies. A FEA-based module has been developed that incorporates microstructural dispersion and interphase relaxation phenomena to simulate the dielectric spectroscopic response of PNCs. The prototype *NanoMine* website (http://nanomine.northwestern.edu:8000) contains basic functionality for data curation (data entry with pre-defined schema) and data exploration (selecting from existing materials and look up data by query). The current beta version is ready for distribution to volunteering academic and industrial research groups for system testing, communal curation and feedback. The *NanoMine* data system is envisioned to interface with the Polymer Design Database (**de Pablo**), being developed to computationally predict structural, thermodynamic and dynamic properties of multiphase functional polymers and block co-polymers systems and the molecular simulation toolkits being assembled at NIST (Phelan (NIST), Khare (NIST), **Luijten**), WebFF and Comsoft Workbench.

Interphase Properties in Polymer Nanocomposites The interphase region between nanoparticles and the matrix polymer, corresponds to a significant volume fraction of PNCs and thus necessitates an accurate understanding of its properties to accurately predict and tailor the properties of PNCs. However, direct experimental measurements of the interphase mechanical and functional properties are scarce in published literature, limiting our understanding of the factors contributing to its development. To this end, direct experimental characterization of the spatial gradients in elastic modulus and viscoelastic mechanical properties in polymer thin films and polymer nanocomposites is being achieved through developments of atomic force microscopy (AFM) based nanoindentation techniques in the vicinity of interfaces, using both model nanocomposite systems (flat 1-d controlled systems) and in situ nanocomposites (**Brinson**, Kolluru (NU), Cheng (NU)). The focus of these experiments has been two-fold: (a) to provide data that will help validate and provide the input required for modeling groups (**Keten, Luijten, de Pablo**) and (b) enable rapid

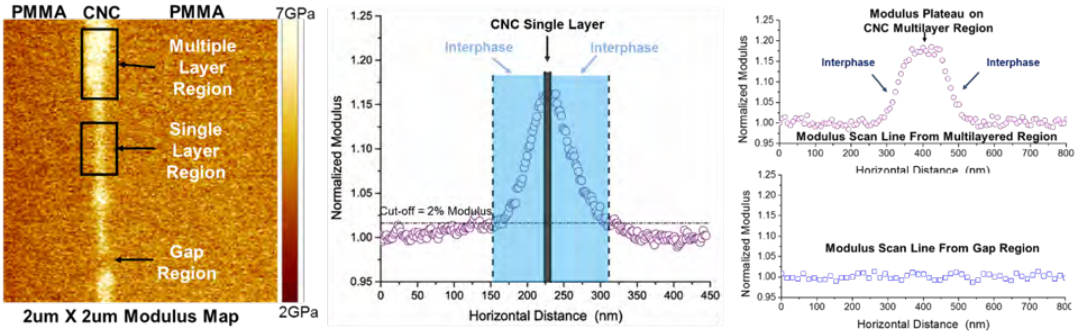


Figure 7.2: AFM-based nanomechanical indentation experiments (**Brinson**) on in-situ nanocomposites

progress in understanding the role of variables such as molecular weight, temperature and strain rate on the interphase mechanical properties, thus bridging the gaps arising from computational limitations on modeling efforts.

Synergistic experimental and modeling efforts on this front have focused on understanding the mechanical behavior of amorphous polymer matrices reinforced with cellulose nanocrystals (CNCs) (preferred for the extremely high modulus and renewable nature). Effects of chemical interactions between the polymer matrix and the filler nanoparticles on interphase glass transition temperatures have been captured through all atomistic molecular dynamic (AA-MD) simulations, the results of which have been used in coarse-grained MD (CG-MD) simulations of model nanocomposite systems to capture the local changes in glass transition temperatures (T_g) of the interphase regions and these results were subsequently used to predict the T_g changes in bulk-scale nanocomposite systems (**Keten**), and are graphically described in Figure 7.1.

Multiscale computational efforts (**Luijten**) are focused on the development of AA- and CG-MD models for poly(ethyleneimine) (PEI) based copolymers. These models, applied to study complexation phenomena, have identified 10-30 fold acceleration in modeling speed, thus ensuring that the systematic computational design of self-assembled nanoparticles can be accomplished in reasonable computational time. These computational models provide two important functions representative of the Materials Genome Initiative: (a) they permit systematic, reliable and efficient computational exploration, and (b) offer mechanistic insight into the interactions between PEI and cellulose, enabling systematic design of additives that alter cellulose surface properties. Internal collaborations are currently underway to understand and guide experimental surface modification of linear and branched PEI. External collaborations with Johns Hopkins University are also underway to pursue the fabrication of PEI-nanoparticles using these models. Complementary experimental work has focused on the development of CNCs with quantified changes in functional surface chemistries and energies (Fox (NIST), Gilman (NIST), Davis (NIST), Woodstock (NIST)), and their incorporation into in-situ nanocomposites with appropriate dispersion for localized AFM measurements (**Brinson**, Fox (NIST)). AFM-based nanomechanical indentation experiments (**Brinson**) on such in-situ nanocomposites, comprised of unmodified CNCs dispersed in PMMA matrix, have successfully identified single and multilayer CNC dispersions and revealed the local elastic modulus gradients in the interphase regions around these CNC layers, as shown in Figure 7.2.

Nanomechanical experiments (**Brinson**) also identify the importance of physical interactions/restrictions experienced by macromolecular chains in the interphase regions of nanocomposites. Studies on model silica-PS nanocomposite system, composed of different monodisperse molecular weights of PS, have identified that increasing molecular weight leads to a gradual increase in the length scale of the interphase region, Figure 7.3, thus suggesting that macromolecular chain length is an important parameter in controlling the development of an interphase region. Collaborative efforts to computationally (**Keten, Luijten**) corroborate the role of macromolecular chain size are currently underway. An important outcome of this collaborative study using low molecular weights polymers will be to provide a perspective on the contribution of molecular weights to the quantitative and qualitative differences between computational (often limited to low molecular weights) and experimental results. Collaboration between experimental (**Brinson**) and computational (**Keten**) research groups has also focused on ensuring the reliability of quantitative mechanical property data obtained by way of a sensitive instrumented indentation methodology. Current experimental efforts are focused on validating recent computational results describing the effects of AFM-tip radius on the measured interphasial mechanical properties, Figure 7.4. The studies on reliability and quantitative accuracy are also being partnered by external collaborations with industrial research partners such as Dow (**Keten**) and Goodyear (**Brinson, Chen**).

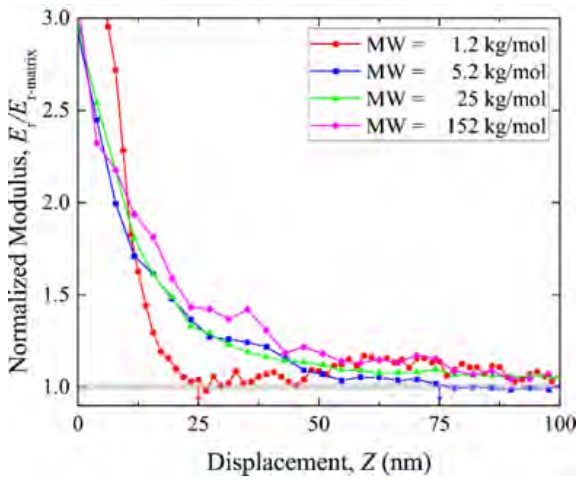


Figure 7.3: Studies on model silica-PS nanocomposite system, composed of different monodisperse molecular weights of PS, have identified that increasing molecular weight leads to a gradual increase in the length scale of the interphase regions

Modeling and Materials Design An overarching objective of the Material Genome Initiative is to develop a materials design chart that details the many parameters contributing to the systematic exploration of the design space and enable the targeted development of novel materials. Figure 7.5, shows a model system-design chart describing the structure-processing-properties interaction in the case of PNCs. Critically, composition and processing conditions affect nanoparticle dispersion and interphase size and properties, which in turn are the major determinants of macroscale response.

Characterization of the dispersion of nanoparticles within the polymer matrix as function of the different process parameters and material constituents (**Brinson, Chen, Keten, Luijten, de Pablo** and Gilman (NIST), Douglas (NIST)) is an important emphasis in this project. Efforts are underway to apply supervised learning techniques (**Chen**) on experimental data (Gilman (NIST)) of carbon nanotube (CNT) dispersion in polymer matrix materials, to identify important microstructural descriptors that can characterize CNT dispersion. These descriptors will then be incorporated into MD simulations (**Keten, Luijten**) and FEA studies (**Brinson, Chen**), to identify the eventually achieve optimal microstructure necessary for targeted properties. It has also been observed that addition of nanoscale particles to polymer solutions can result in complex fluids exhibiting

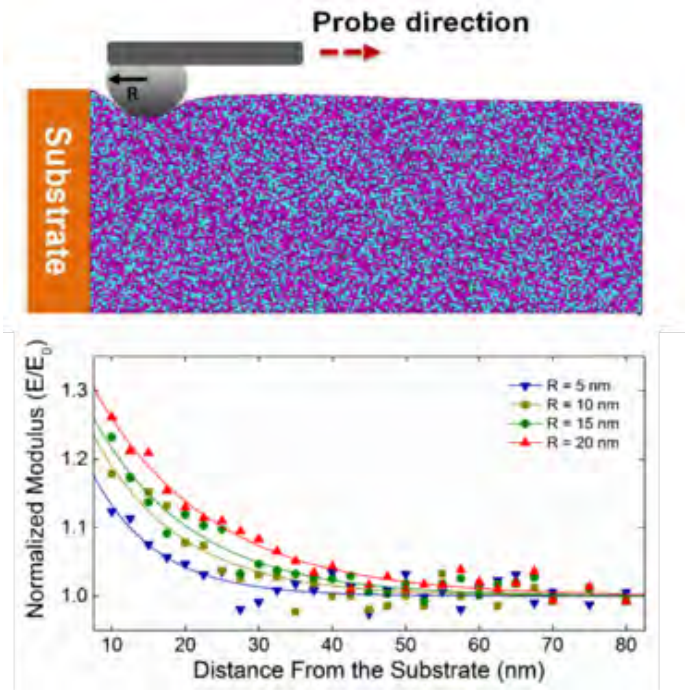


Figure 7.4: Current experimental efforts are focused on validating recent computational results describing the effects of AFM-tip radius on the measured interphasial mechanical properties

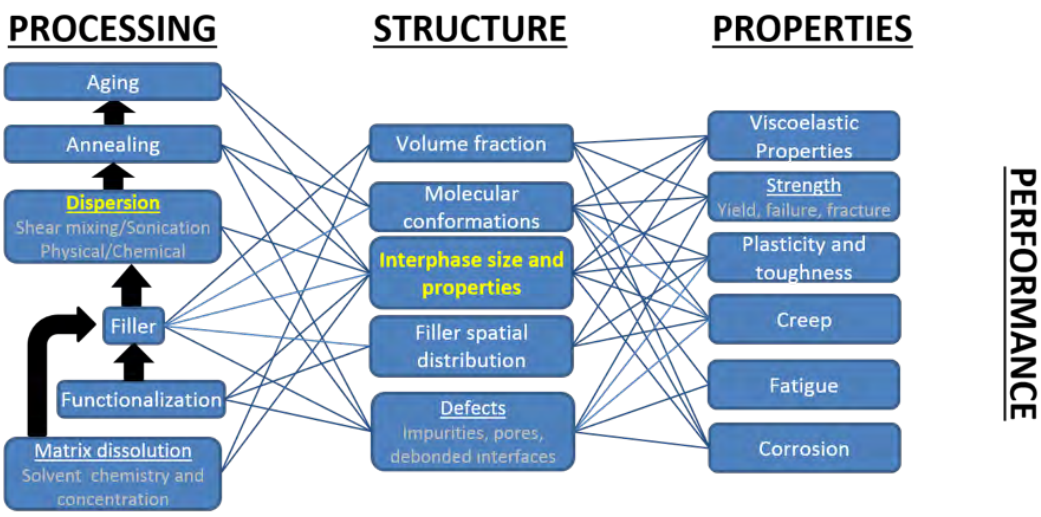


Figure 7.5: A model systems design chart describing the structure-processing-properties interaction for PNCs

non-Einstein-like decrease in viscosity, which has not been explained by any available models. A new particle-based, theoretically informed coarse-grained model (**de Pablo**) for entangled nanocomposites has been proposed to predict and analyze the linear response of PNCs comprised of entangled or unentangled homopolymer matrix. These models have identified that decrease of the viscosity upon addition of nanoparticles is rooted in the increase of contributions to the stress relaxation function arising from the particles, which, for entangled polymers, relax faster than bonded contributions. However, such free volume effects, which are also present in unentangled polymeric liquids, do not change the viscosity in that case because the relaxation time for nanoparticle contributions to the stress relaxation function is comparable to that of bond contributions.

Use of *NanoMine* and associated data resources provide an important pathway to identify the parameters that control the properties of the PNCs, and in turn, enable a comprehensive expansion of the system-design chart presented in Figure 7.5, while other modeling and experimental studies described in the previous section of this report are aimed at directly establishing the interphase structure-property relationships that are currently missing in published literature.

7.4 Collaborations

7.4.1 NIST Collaborations

Characterization of Interphases

*Catherine **Brinson** (NU), Jeffrey Gilman (NIST)*

Brinson and Gilman groups collaborated on coordinating AFM and Flourescence experiments in sample preparation and characterization of polymer-particle interactions.

Identification of Key Filler Descriptors for Carbon Nanotubes

*Wei **Chen** (NU), Chelsea Davis (NIST)*

In collaboration with Davis (NIST), using carbon nanotubes as an illustrative example, **Chen** group will demonstrate the capability of our methods by identifying key filler descriptors from (CNT) experimental images acquired by Davis (NIST), to achieve a better understanding of their impact on properties and perhaps correlations with temperature effects. Statistical characterization and machine learning techniques will be applied to characterize the filler structures and study their relations with properties.

Characterization of Cellulose Nano-crystals

*Wei **Chen** (NU), Sinan **Keten** (NU), Jeffrey Gilman (NIST)*

This collaboration will characterize the dispersion of cellulose nano-crystals (CNC) and use MD simulations to predict the impact of key descriptors such as distribution of minimum distance and compare the results with the experiments of T_g and modules measurements. Two different CNCs with different surface energies and loading weights (VF) will be considered.

Coarse-grained Model Development

*Sinan **Keten** (NU), Jack Douglas (NIST), Frederick Phelan (NIST)*

This collaboration focuses on coarse-grained model development and implementation in WebFF.

7.4.2 External Collaborations

Nanocomposite Characterization and Modeling
*Catherine **Brinson** (NU), Wei **Chen (NU)**, Linda Schadler (Rensselaer Polytechnic Institute)*
This collaboration focuses on fundamentals for understanding polymer nanocomposite interactions and development of design and analysis tools.

Collaborations with The Dow Chemical Company
*Sinan **Keten** (NU)*
This collaboration focuses on determining the reliability and quantitative accuracy of nanoparticle dispersion and interphase size and properties between computational simulations and experiments.

Collaboration with The Goodyear Tire & Rubber Company
*Catherine **Brinson** (NU), Wei **Chen** (NU)*
This collaboration focuses on determining the reliability and quantitative accuracy of nanoparticle dispersion and interphase size and properties between computational simulations and experiments.

Collaboration with Dow Corning
*Jeffrey Gilman (NIST), Catherine **Brinson** (NU)*
Dow Corning is funding a joint NIST/NU project on quantifying interphase formation in glass-polymer composites based on results from the Polymer Matrix Materials use-case group.

7.5 Technology Transfer

Software
NanoMine
R. Zhao, X. Li, C. Brinson, W. Chen, L. Schadler
Link to beta distribution: http://nanomine.northwestern.edu:8000
NanoMine currently can perform basic functionality for data curation (data entry with pre-defined schema) and data exploration (selecting from existing materials and look up data by query). The current beta version is ready for distribution to volunteering academic and industrial research groups for system testing, communal curation and feedback.

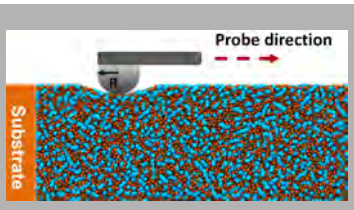
7.6 Publications and Presentations

12 Number of CHiMaD-supported publications in 2015 by Polymer Matrix Materials use-case group. Please see chapter 20 for details. [3, 6, 7, 8, 10, 11, 12, 13, 14, 15, 16, 17]

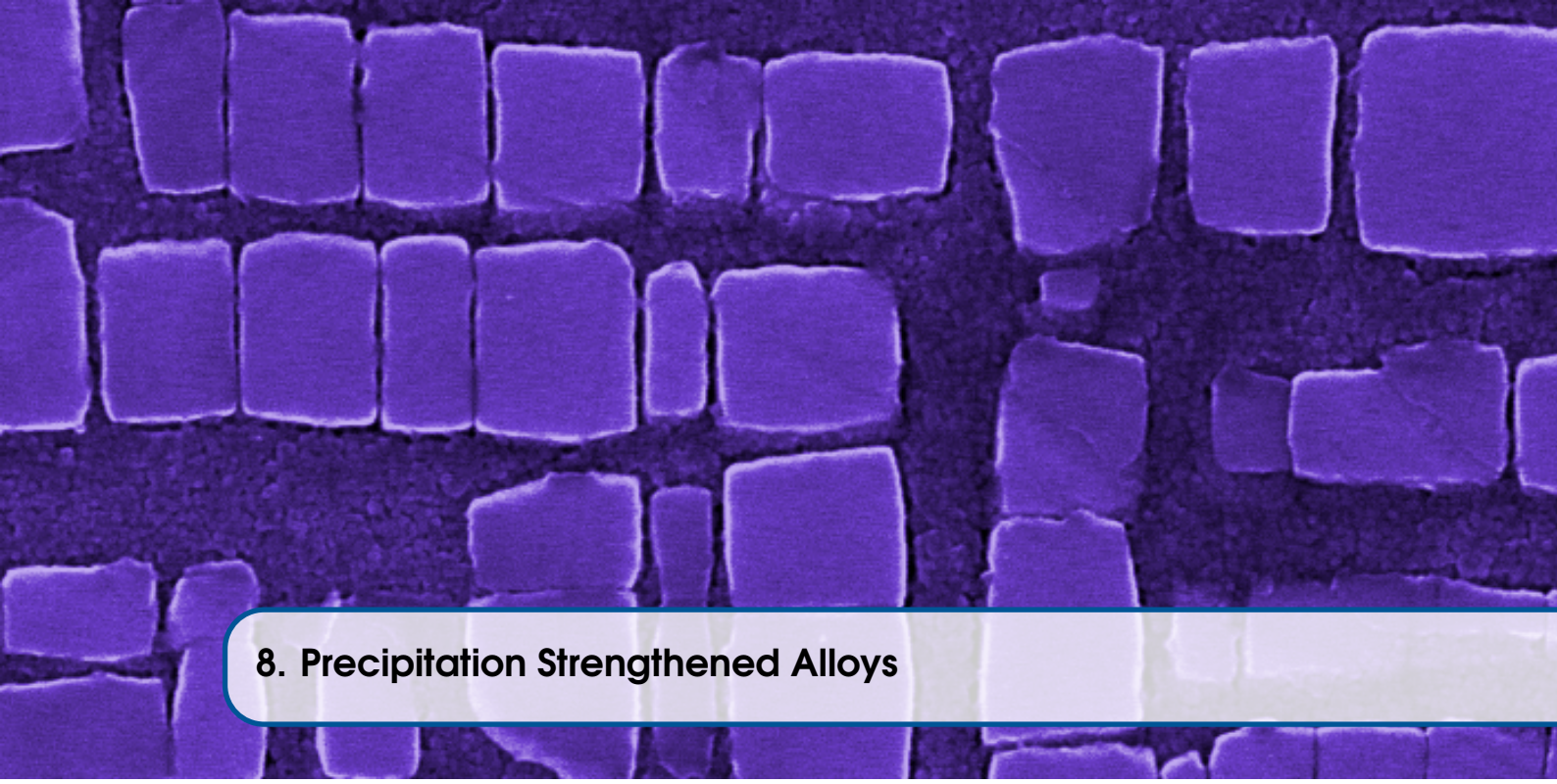
32 Number of presentations on CHiMaD supported research in 2015, please see section 21.6 for the complete list.

7.7 CHiMaD Team

Polymer Matrix Materials Use-Case Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Catherine Brinson Wei Chen Juan de Pablo Sinan Keten Erik Luijten	Principal Investigator Principal Investigator Principal Investigator Principal Investigator Principal Investigator	NU/ME NU/ME UC/IME NU/ME NU/MSE	
Zhiwei Cui	Research Professor	NU/ME	MD simulations for polymer interfaces *(Brinson)*
Pavan Kolluru	Postdoctoral Researcher	NU/ME	Local polymer properties via AFM for Nanocellulose-Polymer interfaces *(Brinson)*
Chen Shao	Postdoctoral Researcher	NU/ME	*(Keten)*
Richard (He) Zhao	Graduate Student	NU/ME	NanoMine *(Brinson)*
Xiaolin Li	Graduate Student	NU/ME	Pocessing-structure relationship of polymer nanocomposites, Nanomine *(Brinson, Chen)*
Yichi Zhang	Graduate Student	NU/ME	Microstructure characterization and reconstruction *(Chen)*
Yongri Su	Graduate Student	UC/IME	Nanocomposites *(de Pablo)*
Xin Qin	Graduate Student	NU/ME	*(Keten)*
Wenjie Xia	Graduate Student	NU/Civil	*(Keten)*
Bobby Sinko	Graduate Student	NU/ME	*(Keten)*
Zonghui Wei	Graduate Student	NU/MSE	Coarse-grained models for PEI *(Luijten)*
Mathias Schmutz	Undergraduate Student	NU/ME	Nanomine data resource curation (Summer Project) *(Brinson)*
Karen Qu	Undergraduate Stundent	NU/ME	Nanomine data resource curation (Summer Project) *(Brinson)*



Header Image: Regenerated from Figure 7.4 by Xia (NU), Keten (NU)



8. Precipitation Strengthened Alloys

Gregory Olson (NU), Wei Chen (NU), Christopher Wolverton (NU), Ankit Agrawal (NU), Alok Choudhary (NU), Yip-Wah Chung (NU), Michael Bedzyk (NU), Wing-Kam Liu (NU), A. Umantsev (FSU), Jason Sebastian (QuesTek), David Snyder (QuesTek), James Saal (QuesTek), Ida Berglund (QuesTek)

Significance

New capabilities in predictive design of precipitation-strengthened alloys are being applied to Co-based superalloys and high-performance Shape Memory Alloys, both employing low-misfit coherent aluminide precipitates closely analogous to the γ- γ' Ni-based superalloys. The Co-based alloys are of interest for both high-temperature creep and fatigue resistance in turbine applications, as well as ambient temperature wear-resistance applications such as aerospace bushings to replace Be-Cu alloys. The shape memory alloys are of high interest for device and actuation applications in medicine, aerospace and automotive sectors where ultrahigh-cycle fatigue is the primary limitation of current alloys; here, efficient precipitation strengthening can eliminate the accommodation slip associated with thermoelastic martensitic transformation, standing as the principal cause of cyclic instability.

8.1 Design Goals

Short-term goals for the Co alloys address ambient temperature applications, where the intrinsic low surface friction characteristics of Co-based alloys makes their precipitation strengthened variants of clear near-term interest as a replacement for Be-Cu aerospace bushing applications of current environmental concern. Long-term goals address high-temperature applications (represented by the system chart of Figure 8.1) where metallic superalloys play a vital role in electrical power generating systems (gas and steam turbines) and jet engines. While achievement of the full set of properties necessary for these applications is an ambitious goal, the potential of the new family of Co-based superalloys to achieve the same strength levels of current Ni-based superalloys, but with a temperature capability 100-150°C higher would enable a major advance in the fuel efficiency of gas

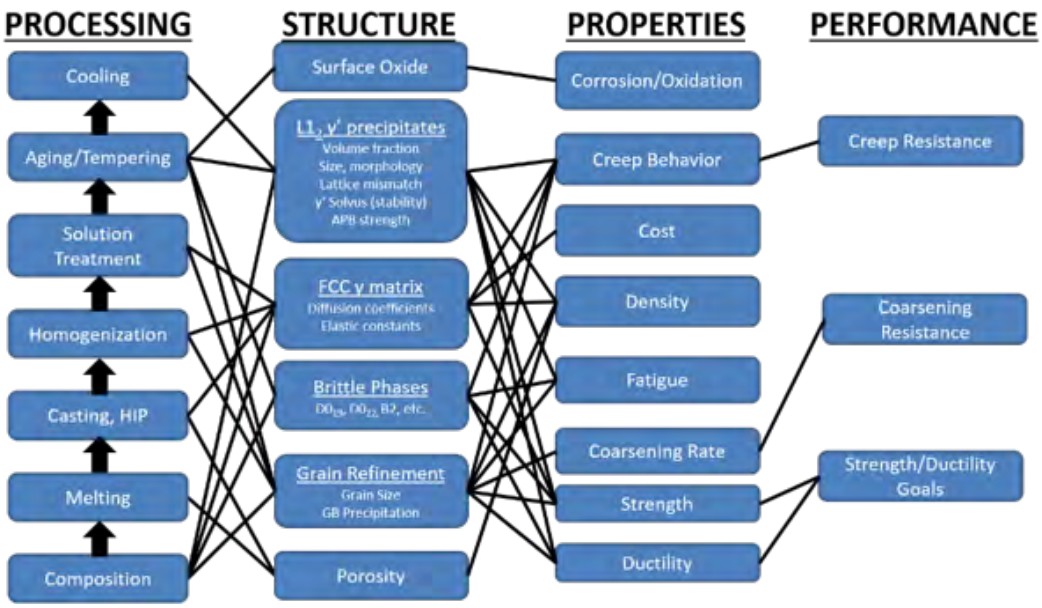


Figure 8.1: Systems design chart of Cobalt Superalloys

turbines and jet engines. In support of new capabilities in additive manufacturing by 3D printing, precipitation-strengthened superalloy research will also address process optimization in the 718+ Ni-based alloy being developed under the DARPA Open Manufacturing program in collaboration with Honeywell.

The breadth of planned databases for Shape Memory alloy design will support both the near-term optimization of high Pd alloys for medical applications favoring high radiopacity and low Ni content for biocompatibility (Figure 8.2), and the longer-term design of lower-cost high Zr alloys to meet the requirements of aerospace and automotive actuators. This will allow the new class of cyclically-stable alloys to have broad technological impact.

8.2 Significant Accomplishments in 2015

Experimentation for Co-alloy fundamental data development Alloy prototypes have been characterized microstructurally via scanning electron microscopy and atom probe tomography. Compression creep testing has been performed for a Co-Al-W-Ti-B alloy for determination of creep activation energy and stress exponents for elevated test temperatures up to 900oC. High temperature yield stresses exceed that of commercial polycrystalline Mar-M247, a Ni-based superalloy.

Co-based CALPHAD Database Development A thermodynamic database for Co-Al-W-Ni-Ti-Ta system including all the binaries is now deliverable. More complex and accurate sublattice models were used in the present database compared to other available multi-component databases. One of the representative accomplishments is the optimization for the Co-W system, as shown in Figure 8.5 and Figure 8.5.

High-throughput Combinatorial Synthesis High-throughput combinatorial synthesis has been successfully implemented in the creation of ternary alloys within any section of the phase diagram. Both the annealing behavior and composition-phase relationship were examined of films composed of Co, Ti, and Ta using high-flux x-rays and other techniques

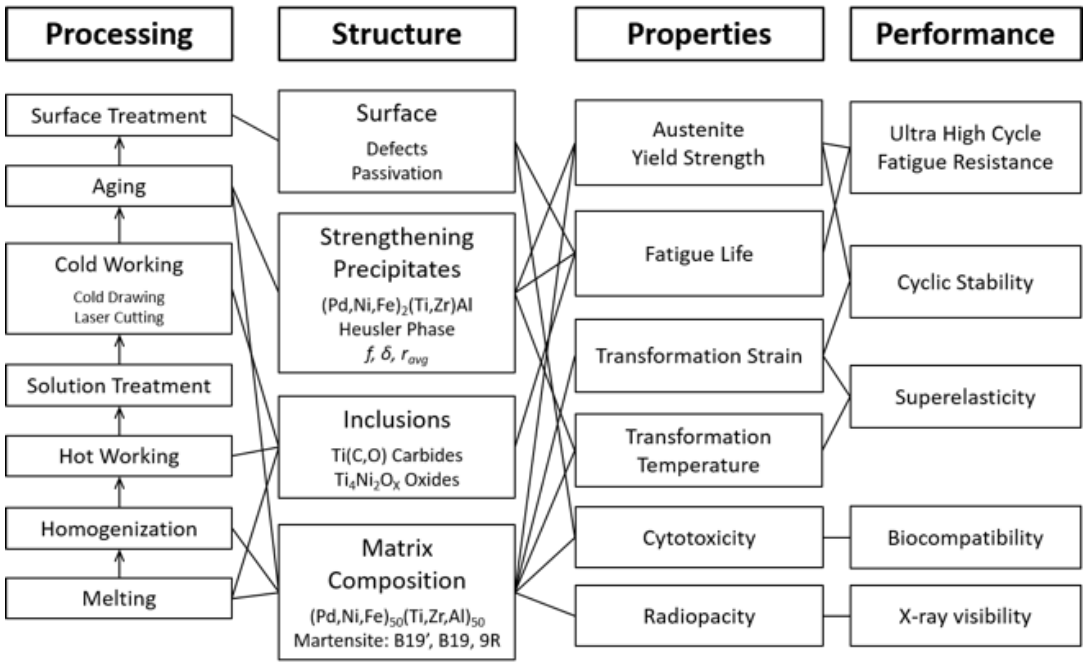


Figure 8.2: Systems design chart of High-Performance Shape Memory Alloys

at Northwestern and the Advanced Photon Source (APS) at Argonne National Laboratory (ANL).

DFT Calculation of Anti-Phase Boundary energies and Diffusion in Co Beginning with accurate benchmark calculations, and based on five-frequency model, accurate diffusion coefficients for Al and W in Co-alloy were calculated. Reliable experimental data are available for comparison and it was determined that several vibrational terms can be accurately approximated or safely ignored. Antiphase boundary (APB) energetics in γ' Co3(Al,W)-based superalloys play a critical role in high-temperature strength. Results indicate a strong dependence of the APB energy on the composition, particularly from the presence of Al-Al bonds across the 010 APB and W-W bonds across the 111 APB. For both APBs, calculations also suggest an energetically favorable segregation of Al to the APB.

High-Performance Shape Memory Alloys Utilizing Fe as an austenite stabilizer, a superelastic Ni-free (Pd,Fe)(Ti,Al) alloy with near-ambient transformation temperatures, low hysteresis, stable thermal and mechanical cycling behavior, and reversible transformation strains of 3.2% was designed. A peak-strengthened superelastic Ni-free prototype demonstrated minimal residual strain and excellent cyclic stability during compressive cycling to 3.5% maximum strain.

Fatigue Nucleation Modeling Interactions were explored between a spherical inclusion and the material's free surface along with several inclusion microstructures reconstructed from 3D imaging. This work determines the distance at which the free surface interacts with an inclusion and the effect of applied strain of surface-inclusion interaction. The effects of inclusion-inclusion interaction, matrix voiding, and matrix strengthening are explored and ranked with regards to their effect on fatigue nucleation.

Integrating CALPHAD and data mining in design for fatigue performance This year a new mechanistic model for calculating Ms temperature was investigated based on statistical

analysis on experimental databases. The new model not only gives better estimates of Ms temperature but also of fatigue strength, which is quite promising and further supports the sensitivity of Ms temperature for fatigue resistance.

*Accelerated Qualification: Accelerated Insertion of Materials (AIM) Methodology*QuesTek has prepared a second 300-lb. heat of the QT-Co aerospace bushing alloy with the target nominal composition, including correctcarbon, produced by means of vacuum induction melting (VIM) followed by vacuum arc remelting (VAR), according to the standard aerospace practice. Experimental data from ten heats were utilized to correct the computational material model. The cumulative density function of strength prediction is obtained based on the bias corrected model to predict the probability of failure. A comparison study was performed between the proposed Bayesian approach and QuesTek?s existing Accelerated Insertion of Materials (AIM) approach in predicting the cumulative density function (CDF) of material properties.

8.3 Research Accomplishments

Experimentation for Co-alloy fundamental data development In collaboration with Lass (NIST), high-temperature Co-alloys were arc melted and then analyzed for compositional and microstructural data by Sauza (NU) and Coakley (NU) from **Dunand** and **Seidman** groups. Several alloy prototypes have been characterized microstructurally via scanning electron microscopy and atom probe tomography. Compression creep testing has been performed for a Co-Al-W-Ti-B alloy for determination of creep activation energy and stress exponents for elevated test temperatures up to 900°C. High temperature yield stresses exceed that of commercial polycrystalline Mar-M247, a Ni-based superalloy. A Co-Ni-Al-Mo-Nb alloy prototype, analyzed by Coakley (NU) and Liu (U) (**Dunand** and **Seidman** Groups), demonstrates comparable solvus and creep strength as ternary Co-9Al-9.8W, but with significantly lower density. Figure 8.3 indicates phase stability of the γ' precipitates in this alloy observed out to 1000 h at 900°C.

Alloys developed in collaboration with Lass (NIST) included two Co-Ni-Al-Ti-Mo-Nb-Ta alloys, with one containing W and one without. The alloy containing W was vacuum induction melted (VIM) and recast as a single crystal by Alcoa-Howmet. The alloy was further studied during beamtime at Oak Ridge National Lab of in-situ diffraction during creep. The alloy without W was studied for a unique microstructure consisting of parallel, directionally coarsened γ'. Atom probe tomography was performed, seen in Figure 8.4, demonstrating Ni, Al, Ti, Mo, Nb, and Ta all partition to the γ' phase, while only Co partitions preferentially to γ.

Co-based CALPHAD Database Development Efforts to establish a multi-component thermodynamic database (CALPHAD), for the design of Co-based superalloys, continue to progress through the efforts of Wang (NIST/CHiMaD Postdoctoral Fellow), Xiong (NU) and **Olson** (NU). The Co-Al-W-Ni-Ti-Ta system is of primary interest. The Co-Al, Co-W, Co-Ta, Al-W and Al-Ni systems were reviewed and re-optimized by cooperating density functional theory (DFT) calculations. The γ' phase was described as metastable phase in Co-Al, Co-W and Al-W systems. A thermodynamic database for Co-Al-W-Ni-Ti-Ta system including all the binaries is now deliverable. More complex and accurate sublattice models were used in the present database compared to other available multi-component databases. One of the representative accomplishments is the optimization for the Co-W system, as shown in Figure 8.5 and Figure 8.6.

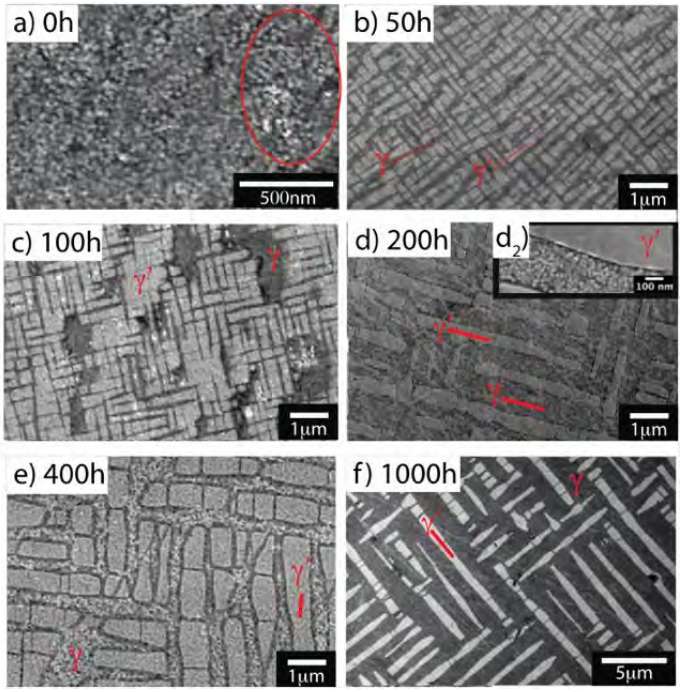


Figure 8.3: SEM micrographs of Co-30Ni-10Al-4Mo-2Nb (at.%) alloy a) homogenized at 1300°C for 24 h followed by a water quench. b-f were further aged at 900°C, followed by water-quenching, for b) 50 h, c) 100 h, d) 200 h, e) 400 h and f) 1000 h.

High-throughput Combinatorial Synthesis High-throughput combinatorial synthesis, led by **Chung** and **Bedzyk**, has been successfully implemented in the creation of ternary alloys within any section of the phase diagram. This was achieved by combining DC magnetron sputtering with photolithography to create a two-dimensional array of points covering a selected composition range. Both the annealing behavior and composition-phase relationship were examined of films composed of Co, Ti, and Ta using high-flux x-rays and other techniques at Northwestern and the Advanced Photon Source (APS) at Argonne National Laboratory (ANL). Single crystal sapphire substrates were used in this investigation due to their distinct XRD peaks for ease of filtering and thermal stability - there is no observable substrate-film interaction even after extended annealing at 800°C.

Because of the refractory nature of component elements, the diffusion kinetics are expected to be relatively slow. At annealing temperatures of 600-700°C, metastable phases are formed after 3-6 hours. Annealing at 800°C for six hours appears sufficient to yield stable, homogenized phases as shown in Figure 8.7.

Figure 8.8 shows three sample XRD patterns from alloys with different compositions after extended annealing at 800°C. Subtle changes in the diffraction pattern are observed as a function of composition, indicating evolution of phases. To establish reliability of this approach to alloy synthesis, this method was used to prepare Co-Ti-Ta single-component and binary alloys previously reported. In addition to verifying agreements with established databases, our studies reveal the formation of metastable phases not shown in standard binary phase diagrams when annealed at shorter times. The project has received commendation for the experimental design from ANL-APS.

DFT Calculation of Anti-Phase Boundary energies and Diffusion in Co Naghavi (NU) and **Wolverton** focused on: energetic calculations of binary Co-alloys and compounds,

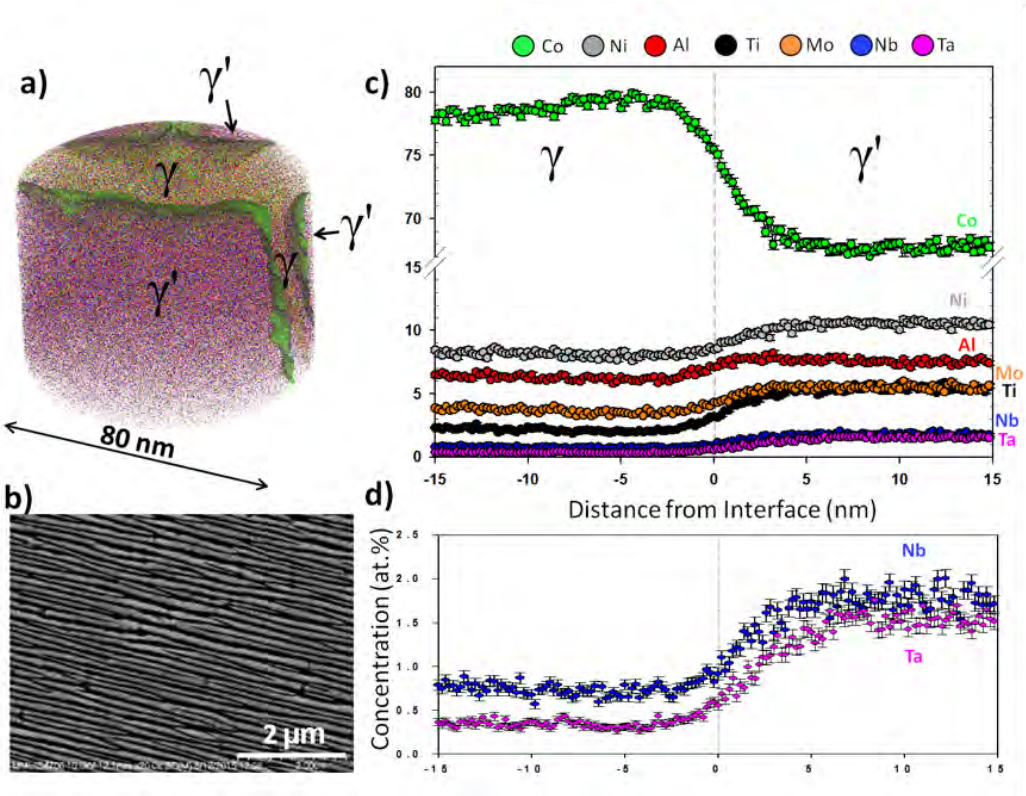


Figure 8.4: Characterization of Co-10Ni-7Al-4Ti-5Mo-1Nb-1Ta (at.%) alloy aged for 24 h at 900°C a) local electrode atom probe (LEAP) reconstruction containing γ' precipitate and γ channels, delineated by a 72% Co isosurface b) SEM micrograph (courtesy of Lass (NIST)) demonstrating elongated precipitate morphology c) proximity histogram demonstrating various elemental concentrations as a function of distance from the γ/γ' interface d) magnified portion of (c) to demonstrate the partitioning of Nb and Ta preferentially to γ'.

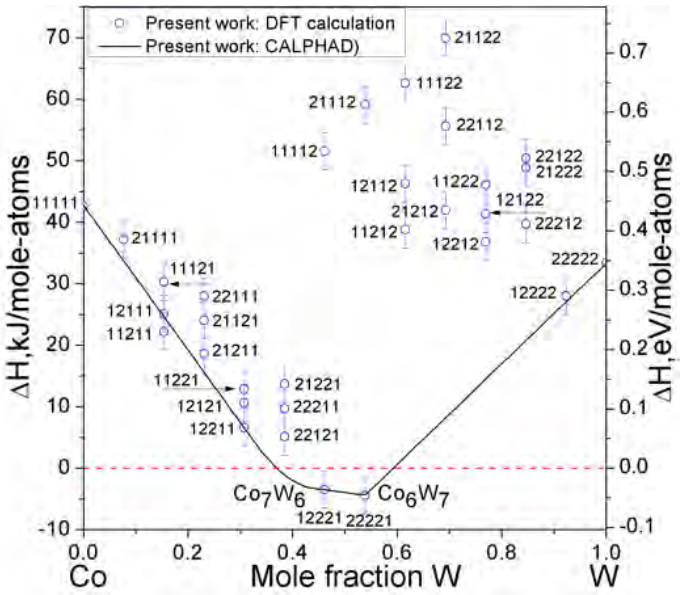


Figure 8.5: Calculated CALPHAD enthalpy of formation of the μ phase compared to first-principles (FLAPW) results. The reference state is Hcp Co (non-magnetic) and Bcc W. The open blue circles are the calculated enthalpy of formation for all the end-members of μ phase. The composition of each end-member is presented by a five-digit number like 22122, where 1 corresponds to Co and 2 to W, and the order of digits reflect the occupancy of the corresponding sublattices in the following order: Co1(3a)-W1(6c1)-W2(6c2)-W3(6c3)-Co2(18h). For example, 12221 corresponds to the nominal μ-phase Co7W, 22221 - the "new'" μ-phase Co6W7. The error bar for the FLAPW results is $\pm$3kJ/mole-atoms (or 0.03 eV/mole-atoms).

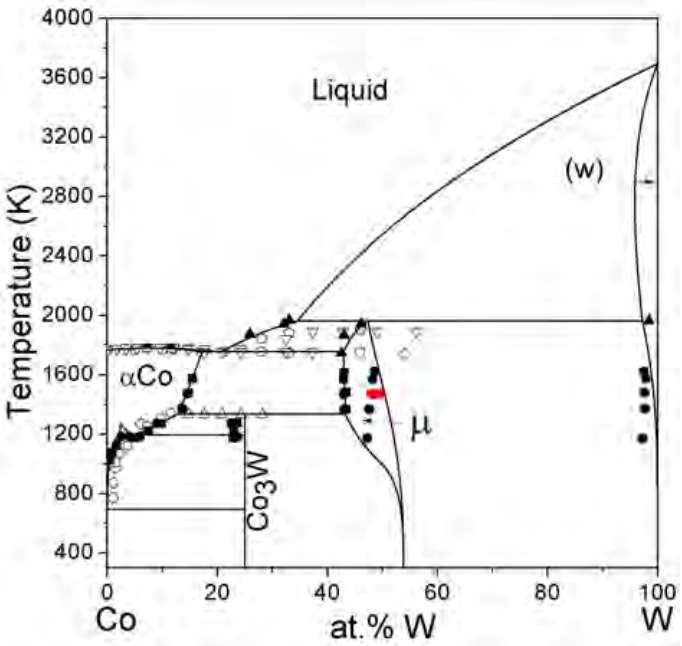


Figure 8.6: Calculated Co-W phase diagram compared with experimental data

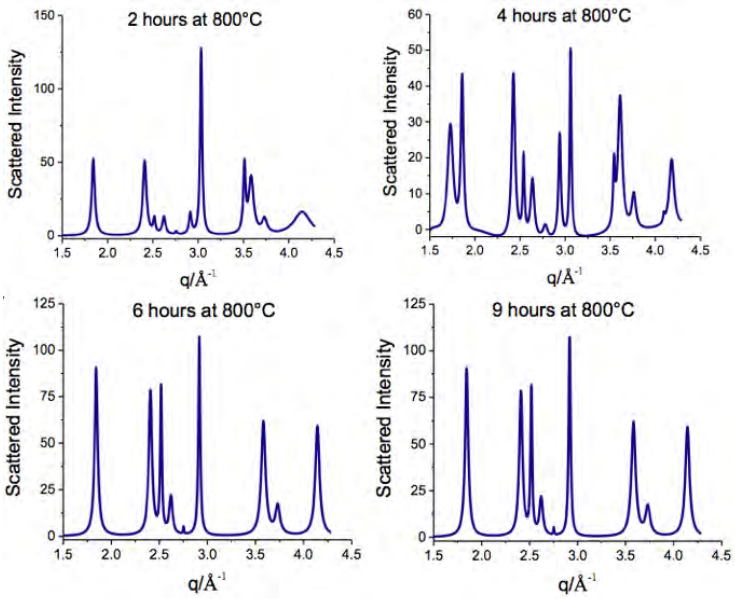


Figure 8.7: Evolution in the x-ray diffraction pattern of $Co_{81}Ti_6Ta_{13}$ as a function of annealing. The sample was first annealed for 3 hours at 600°C, followed by an annealing at 800°C for (a) 2 hours, (b) 4 hours, (c) 6 hours, (d) 9 hours. The Final two anneals(c), (d), did not bring about significant changes in the observed peaks. The peaks were baseline-subtracted and fitted using IgorPro

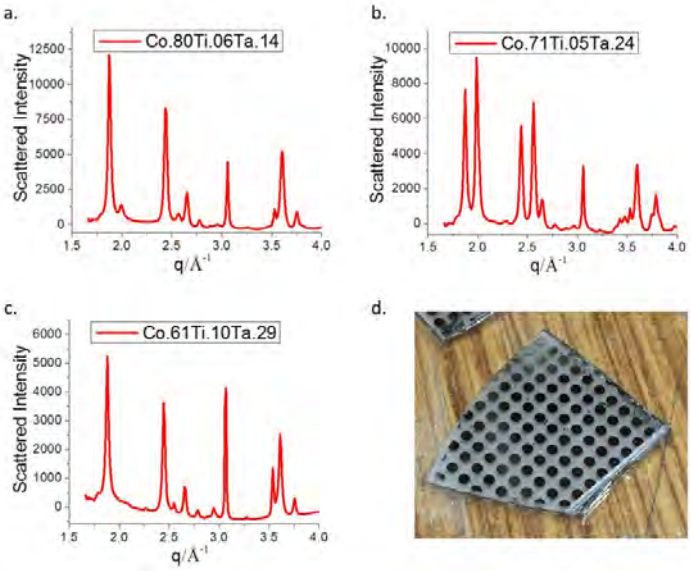


Figure 8.8: X-ray diffraction patterns from three different Co-Ti-Ta alloys annealed at 650°C for 9 hours: (a) $Co_{80}Ti_6Ta_{14}$, (b)$Co_{71}Ti_5Ta_{24}$, (c)$Co_{61}Ti_{10}Ta_{29}$, and (d) the 2D array of Co-Ti-Ta ternary alloy samples. The peaks were linear-baseline subtracted in IgorPro

diffusion process in Co alloys, and Anti-phase boundary (APB) calculations of Co3(Al,W) compounds. The goal in energetic calculations of binary Co-alloys is to build a database of solute-vacancy binding energies in fcc-cobalt based on accurate first-principles density functional calculations. To do so, the solute-vacancy binding energy, dilute mixing energy, dilute volume of mixing, and solubility enthalpy of 27 substitutional solutes in fcc-Co are calculated using Density Functional Theory. Including all of the alloying elements used in Co-based superalloys which cover most 1st-3rd transition metal elements - except groups 3 and 12- together with Si, C, B and Al, it was discovered that energetic parameters such as solute-vacancy binding energy vary systematically across the transition metals. This behavior is explained by a band-filling effect, known as Friedel's model. The observed trend can aid experimentalists by estimating energetic parameters of transition metals prior to making any measurements or calculations.

In regards to diffusion, the ultimate goal is to build a diffusion coefficient database of transition metals in cobalt. However, this is a difficult (probably impossible) task due to the high computational costs of an exact diffusion calculation. Simplified methods are required. To simplify such calculation, key terms must be approximated in the diffusion model without losing much accuracy. Beginning with accurate benchmark calculations to analyze each term carefully, and based on five-frequency model, accurate diffusion coefficients for Al and W in Co-alloy were calculated. Reliable experimental data are available for comparison and it was determined that several vibrational terms can be accurately approximated or safely ignored.

Antiphase boundary (APB) energetics in γ' Co3(Al,W)-based superalloys play a critical role in high-temperature strength. APBs can affect the magnitude and temperature-range of the yield strength anomaly. APBs in L12 Co3(Al,W) γ' are particularly complex due to the presence of the metal mixing on the Al/W sublattice, which introduces additional degrees of freedom to APB behavior, such as Al/W composition and configuration local to the APB. The behavior of APBs in L12 Co3(Al,W) were explored with density functional theory. Results indicate a strong dependence of the APB energy on the composition, particularly from the presence of Al-Al bonds across the 010 APB and W-W bonds across the 111 APB. For both APBs, calculations also suggest an energetically favorable segregation of Al to the APB. Therefore, future Co alloy design criteria can include alloying elements with preferential segregation to the APB over that of Al to tune the APB energy (and the behavior of the yield strength anomaly). Furthermore, the unique behavior of Al-Al and W-W bonds in the 010 and 111 APB's, respectively, indicate the possibility of preferentially modifying one APB over another with alloying.

High-Performance Shape Memory Alloys Frankel (NU), supervised by **Olson**, focused on the development of biocompatible, precipitation-strengthened fatigue resistant PdTi-based SMAs for biomedical applications (as representedin the system chart of Figure 8.2). Controlled precipitation of nanoscale, low-misfit, L21 Heusler aluminides can provide effective strengthening. Phase relations, precipitation kinetics, transformation temperature, transformation strain, cyclic stability, and mechanical properties were characterized in both Ni-free (Pd,Fe)(Ti,Al) and low-Ni high-strength *hybrid* (Pd,Ni)(Ti,Zr,Al) systems. Atom probe tomography was employed to measure phase compositions and particle sizes used to calibrate LSW models for coarsening kinetics and Gibbs-Thompson models for composition trajectories for systems under evolving unstable equilibrium. Mechanical and thermal cyclic stability were investigated using compression testing and differential scanning calorimetry. Mechanical properties were characterized using room temperature

and high temperature Vickers microhardness as well as nanoindentation.

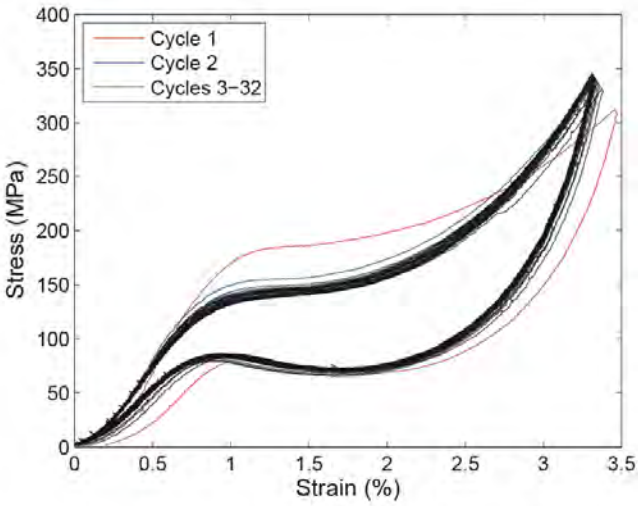


Figure 8.9: Stress-strain response from compressive fatigue testing performed on a Ni-free $Pd_{42.2}Fe_{7.8}Ti_{44}Al_6$ alloy at T=A_f+25°C.

Utilizing Fe as an austenite stabilizer, a superelastic Ni-free (Pd,Fe)(Ti,Al) alloy with near-ambient transformation temperatures, low hysteresis, stable thermal and mechanical cycling behavior, and reversible transformation strains of 3.2% was designed. A peak-strengthened superelastic Ni-free prototype demonstrated minimal residual strain and excellent cyclic stability during compressive cycling to 3.5% maximum strain (Figure 8.9). Due to Pd softening, the addition of Zr was considered to improve strength in a low-Ni *hybrid* (Pd,Ni)(Ti,Zr,Al) alloy. Aging studies at 600°C resulted in unusually fast coarsening kinetics, while low-temperature aging studies at 500-530°C revealed the presence of a third Zr-rich phase in association with the matrix and Heusler phase. A strengthening study on a non-transforming hybrid prototype showed lower than expected precipitation strengthening at 600°C but significant strengthening when aged at 500°C due to high volume fractions of the Zr-rich phase. Transformation temperatures, transformation strain, and cyclic stability were characterized in a set of transforming hybrid prototypes.

Fatigue Nucleation Modeling The potency of nucleating inclusions is an important factor in the fatigue life of shape memory alloys. For other alloy systems, computational models have proven an effective means of determining the relationship between inclusion features and fatigue life. Moore (NU) under the supervision of **Liu** extended a subset of those models, based on crystal plasticity, to examine the role inclusion microstructure plays in the fatigue life of NiTi alloys using a computational model based on crystal plasticity. We explore the interaction between a spherical inclusion and the material's free surface along with several inclusion microstructures reconstructed from 3D imaging. This work determines the distance at which the free surface interacts with an inclusion and the effect of applied strain of surface-inclusion interaction. The effects of inclusion-inclusion interaction, matrix voiding, and matrix strengthening are explored and ranked with regards to their effect on fatigue nucleation.

Three meshes were created based on the mesh shown in the Figure 8.10. These meshes modeled two inclusions with a void, two inclusions without a void and one inclusion (the largest) without a void. Preliminary results show a three to ten times increase in fatigue life when voiding does not occur. This confirms that it is the debonding and voiding that is increasing the fatigue crack nucleation potency around typical inclusion stringers rather than mechanical interaction. Thus, process optimization to reduce voiding and debonding will increase fatigue performance, and stringers formed from fracturing inclusions will be more detrimental than naturally occurring clusters of unfractured inclusions. However,

the increase is fatigue life found from removing voiding is still small as compared to the fatigue life improvement caused by increasing NiTi matrix yield strength by 50%. Moore (NU) defended his doctoral thesis in 2015 and a manuscript has been submitted for publication.

At length scales where dislocation plasticity becomes size dependent, nonlocal mechanics models can provide greater simulation accuracy. **Umantsev** has collaborated with QuesTek in assessing prior literature for adaptation of the Phase-Field Method to the micromechanics of fatigue.

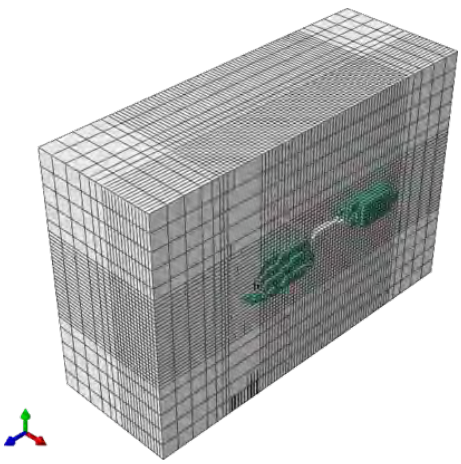


Figure 8.10: Representative mesh for modeling two inclusions

Integrating CALPHAD and data mining in design for fatigue performance A collaboration of **Agrawal, Choudhary, Olson**, and Xiong (NU), aims to design an effective interface between data mining techniques and CALPHAD methodology for materials genomic design. The research studies are performed on the carbon steels fatigue strength data with raw data sets obtained from experiments provided by NIMS (National Institute for Materials Science, Japan). This year a new mechanistic model for calculating Ms temperature was investigated based on statistical analysis on experimental databases. The new model not only gives better estimates of Ms temperature but also of fatigue strength, which is quite promising and further supports the sensitivity of Ms temperature for fatigue resistance. Building on the success of our CHiMaD demonstration of the integration of data analytics with CALPHAD knowledge, QuesTek has won a $3.6 million DARPA-SIMPLEX multi-institutional project with an NU team based in CHiMaD, applying this approach in the computational design of thermoelectric materials.

Accelerated Qualification: Co-alloy Process Optimization QuesTek (**Olson, Sebastian, Snyder, Saal, Berglund**) successfully cast a 300-lb. heat of QT-Co with the target nominal composition, including carbon, produced by means of vacuum induction melting (VIM) followed by vacuum arc remelting (VAR), according to the standard aerospace practice (Figure 8.11). Following delivery of the as-cast ingot, a thorough homogenization and hot working optimization was executed - including heat treatment validation studies and Gleeble thermo-mechanical simulations. Using light-optical microscopy and electron microprobe analysis (EMPA), the as-VAR microsegregation was analyzed for dendrite arm spacing and chemical inhomogeneity. The as-cast analysis is used to calibrate DICTRA simulations to determine an optimal homogenization procedure.

Modeling activities at QuesTek have centered on achieving higher yield strength in QT-Co through simulation-driven thermal process optimization. In particular, homogenization treatment optimization has addressed more efficient homogenization and a reduction in the anneal time. To reduce the isothermal temper time of 72 hours to peak strength, an experimental aging study was coupled with DICTRA solidification and homogenization simulations to identify novel temper schemes, including a two-step process. The 1050°C homogenization scheme has been verified experimentally, providing adequate dissolution of the as-cast dendritic structure. These CALPHAD simulations employed previously optimized thermodynamic and kinetic databases from Year One activities. With the correct

carbon content established in this second heat, the designed TiC-based grain refinement should allow achievement of the yield strength goal.

Figure 8.11: As cast 300-lb VIM/VAR heat of QT-Co

QuesTek has obtained an Air Force SBIR contract to aid the qualification of the QT-Co bushing alloy, and has submitted a proposal to the Environmental Security Technology Certification Program (ESTCP) for further qualification testing. A proposal has also been submitted to the National Institute of Health (NIH) for validation testing of the PdTi-based shape memory alloy for medical applications.

Accelerated Qualification: Accelerated Insertion of Materials (AIM) Methodology Collaboration continues between QuesTek and **Chen**. Several research tasks have been completed, including the development of a powerful metamodeling approach based on the Gaussian Process Regression (GPR). GPR can replace the time-consuming computational material models currently in use, such as the process-structure-property simulations of QuesTek's Ferrium M54 steel. The metamodel uses input variables that include chemical compositions and processing temperature profile while the output is the prediction of material properties such as the ultimate tensile strength. Secondly, a Bayesian model bias correction approach was employed to integrate information from both material simulation models and the experimental data in predicting the probability that material strength is smaller than a critical threshold. Experimental data from ten heats were utilized to correct the computational material model. The cumulative density function of strength prediction is obtained based on the bias corrected model to predict the probability of failure. Figure 8.12 shows a comparison study between the proposed Bayesian approach and QuesTek's existing Accelerated Insertion of Materials (AIM) approach in predicting the cumulative density function (CDF) of material properties. Our study illustrates the advantage of the Bayesian approach with its capability of providing the 95% confidence bounds of CDF curves by taking into account the epistemic uncertainty due to the lack of experimental and simulation data while the AIM approach provides the prediction of the CDF profile as shown in Figure 8.12 without uncertainty quantification. This research provides an approach that can quantitatively assess a material property's probabilistic behavior by taking into account the epistemic uncertainty due to the lack of experimental and simulation data. The work is significant in enhancing the confidence of using the computational materials design approach, with ultimate application in qualification of the new Co-alloys.

8.4 Collaborations

8.4.1 CHiMaD Collaborations

Scalable Frameworks for Mesoscale Modelling

*David **Dunand** (NU), David **Seidman** (NU), Olle **Heinonen** (ANL)*

Discussions were initiated with **Heinonen** and Josikaari (ANL), on the subject of adapting their scalable framework for mesoscale modeling of microstructural evolution to the

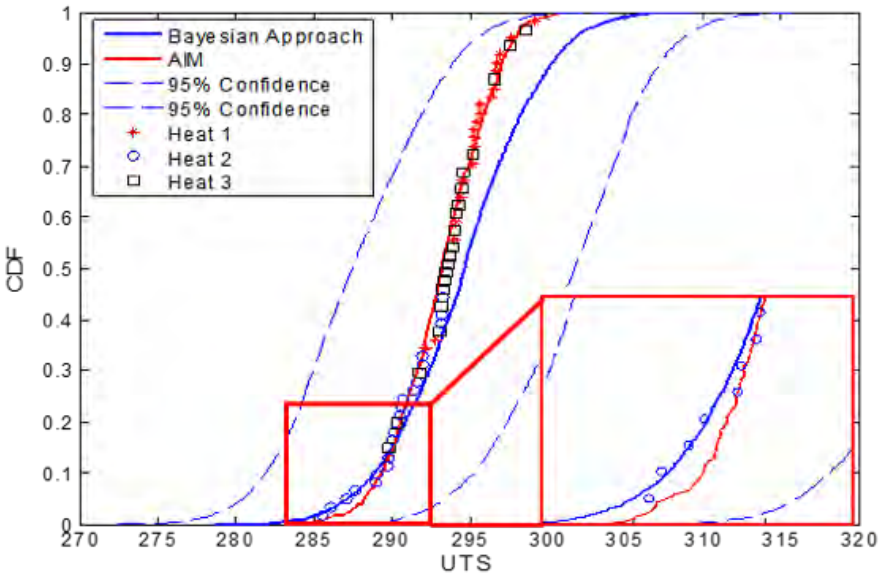


Figure 8.12: Bayesian approach vs. AIM approach in predicting the probability that the material strength is lower than 280 psi

problem of γ'-strengthened Co-base superalloys, with the goal of modeling the coarsening and rafting behavior of the strengthening γ' to inform future alloy and process design.

High-throughput DFT Methods for Alloy Design

*David **Dunand** (NU), David **Seidman** (NU), Christopher **Wolverton** (NU)*

Discussions with **Wolverton**, Naghavi (NU), and Hegde (NU) to refine properties/areas of interest where high-throughput DFT methods might inform future experimentation/alloy design or vice versa. Students and postdoctoral researchers from both groups attended the fall materials design workshop, where they collaborated on a system design chart for γ'-strengthened high-temperature Co alloys.

Nucleation: Parallel Computing using ANL's Supercomputer 'Blues'

*Alexander Umantsev (FSU), Olle **Heinonen** (ANL)*

Due to the nature of rare-event processes, simulation of nucleation requires long computational time. This brings up a need in a fast computing facility. ANL's "Blues" Supercomputer was utilized for the project.

8.4.2 NIST Collaborations

Phase stability of Co-Alloys

*Christopher **Wolverton** (NU), Ursula Kattner (NIST), Carelyn Campbell (NIST)*

There is a strong communication between the **Wolverton** group with Kattner (NIST) and Campbell (NIST).

Co-alloy Microanalytical Characterization

*David **Dunand** (NU), David **Seidman** (NU), Eric Lass (NIST), Kil-Won Moon (NIST), Maureen Williams (NIST)*

The NIST experimental group led by Lass (NIST) arc-melted a series of prototype Co alloys, in which we are collaborating on further evaluation. Information obtained from these alloys (e.g. γ' stability, composition, size, phase fraction) will serve as the basis for

the next iteration of alloy design. Regular teleconferences occur between groups to update on progress and discuss next steps.

8.4.3 External Collaborations

AIM Methodology

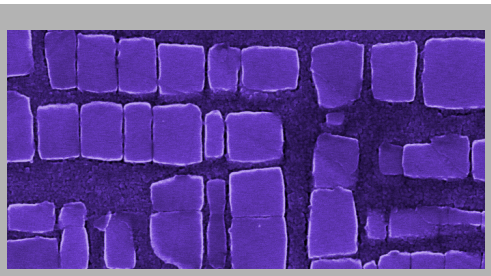
*Wei **Chen** (NU), David **Snyder** (QT), Jiadong Gong (Questek Innovations)*

Chen group collaborated with **Snyder** (QT) and Gong (QT) to retrieve both simulation and experimental data for the supper alloy. **Chen** group analyzed the ten heats data with 21 lots and extracted the important time-history thermal information for each experimental data.

8.5 Publications and Presentations

10 Number of CHiMaD-supported publications in 2015 by Precipitation-strengthened Alloys use-case group. Please see chapter 20 for details. [18, 19, 20, 21, 22, 23, 24, 25, 26, 27]

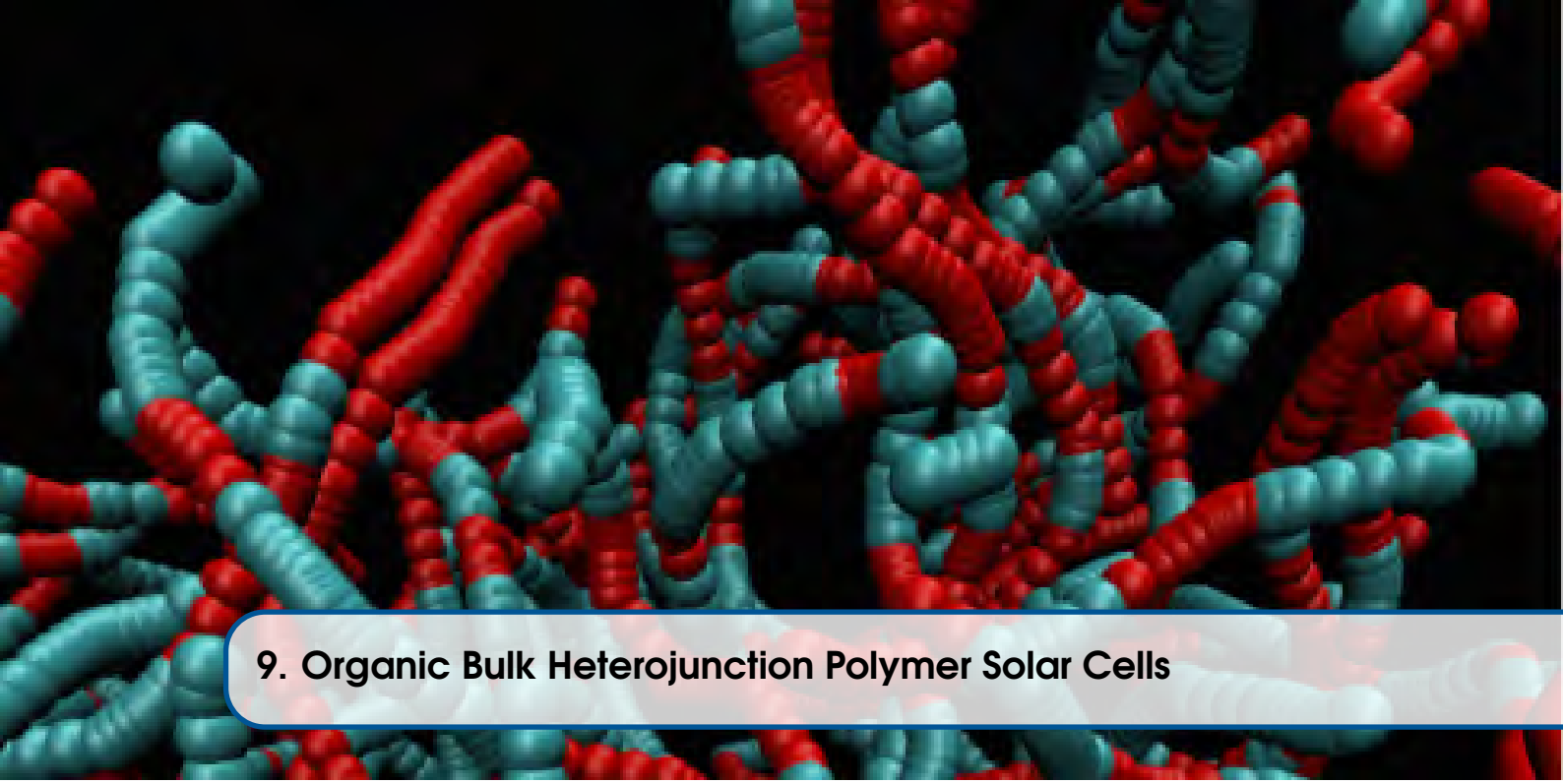
10 Number of presentations on CHiMaD supported research in 2015, please see section 21.7 for the complete list.



Header Image: Scanning electron micrograph depicting cuboidal (L12) γ'-precipitates surrounded by channels of (f.c.c.) γ-matrix in an aged Co-Al-W-Ti-B alloy (D. Sauza, D. Dunand, D.Seidman).

8.6 CHiMaD Team

Precipitation-Strengthened Alloys Use-Case Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Gregory Olson	Principal Investigator	NU/MSE	
Wei Chen	Principal Investigator	NU/ME	
Christopher Wolverton	Principal Investigator	NU/MSE	
Ankit Agrawal	Principal Investigator	NU/EECS	
Alok Choudhary	Principal Investigator	NU/EECS	
Yip-Wah Chung	Principal Investigator	NU/MSE	
Michael Bedzyk	Principal Investigator	NU/MSE	
Wing Kam Liu	Principal Investigator	NU/ME	
Alexander Umantsev	Principal Investigator	FSU/PHY	
Jason Sebastian	Principal Investigator	QT	
David Snyder	Principal Investigator	QT	
James Saal	Principal Investigator	QT	
Ida Berglund	Principal Investigator	QT	
Peisheng Wang	NIST/CHiMaD Postdoc	NU/MSE	Co-Alloy database development *(Chen)*
Wei Xiong	Research Associate	NU/MSE	materials design *(Olson)*
Zequn Wang	Postdoctoral Researcher	NU/ME	*(Chen)*
Shahab Naghavi	Postdoctoral Researcher	NU/MSE	*(Wolverton)*
James A. Coakley	Postdoctoral Researcher	NU/MSE	Co-alloys *(Seidman/Dunand - EU Marie Curie Fellow)*
Daniel Sauza	Graduate Student	NU/MSE	Co-Alloys *(Dunand/Seidman)*
Dana Frankel	Graduate Student	NU/MSE	Shape Memory Alloys *(Olson - Graduated Ph. D.)*
John Moore	Graduate Student	NU/ME	Fatigue *(Liu - Graduated Ph. D.)*
Qinyuan Liu	Graduate Student	NU/MSE	Fatigue *(Dunand/Seidman - Left CHiMaD program)*
Cameron Gross	Graduate Student	NU/MSE	High Throughput Combinatorial Synthesis and Analysis of Ternary Alloys *(Chung/Bedzyk)*
Logan Ward	Graduate Student	NU/MSE	Data Mining *(Wolverton)*
Janak Thapa	Graduate Student	NU/MSE	High Throughput Combinatorial Synthesis and Analysis of Ternary Alloys *(Chung/Bedzyk)*
Chuan Liu	Graduate Student	NU/MSE	SMA for biomedical applications *(Olson)*
Orion Kafka	Graduate Student	NU/ME	Fatigue *(Liu)*
Ding-Wen (Tony) Chung	Graduate Student	NU/MSE	Co-alloys *(Dunand/Seidman)*
Nathaniel Murry	Undergraduate Student	FSU/PHY	Additive Manufacturing *(Umantsev)*
Shardai Johnson	Undergraduate Student	FSU/PHY	Additive Manufacturing *(Umantsev)*
Furaha Ive	Undergraduate Student	FSU/PHY	Nucleation *(Umantsev)*



9. Organic Bulk Heterojunction Polymer Solar Cells

Luping Yu (UC), Juan de Pablo (UC), Guilia Galli (UC), Tobin Marks (NU)

Significance

Bulk heterojunction organic solar cells (OSCs) represent an alternative solar energy harvesting system, which is pursued by numerous research groups world-wide. Commercial products are starting to appear in the market from several companies. This use-case group is addressing critical issues that affect the performance of OSC devices through materials design and synthesis to test new structure/function ideas, exploring new means of morphological control and its influence on OSC performance, new approaches to device optimization, data collection/analysis on new formulations and device characteristics, and on structure/property relationships. New electron donors or acceptors exhibiting superior photovoltaic properties are being developed, and their synergistic interactions are being studied. General rules for designing new polymers for use as charge relays or energy harvesting antennae in ternary OSCs are also being investigated. In close coupling to these experimental efforts, new theoretical methods are being developed to elucidate key electronic processes (electronic excitation, charge separation and transport) in our champion polymer systems and ternary polymer solar cells. To this end, large-scale modeling approaches are also being developed to simulate the morphology formation, polymer chain aggregation, and ways to control them. These studies are also closely coupled with efforts by NIST scientists to fully utilize their expertise in structural and morphological characterization of CHiMAD materials. These new materials and the basic knowledge gained will deepen our understanding of structure/property relationships and accelerate the development of OSCs towards more efficient and cost-effective commercial products.

9.1 Design Goals

The main design goal of the Organic Bulk Heterojunction Polymer Solar Cells use case group is to arrive at all-organic solar cells with reproducible efficiencies that are well above those of currently known for organic thiophene-based materials (ca. 8%). In long term, a

key aim of this group is to arrive at all-polymer organic photovoltaic materials that will obviate the need for fullerenes. The development of OPV materials to date has largely followed an Edisonian approach. This group seeks to identify key molecular and structural descriptors of performance which may be used in the future to rationally design improved materials for next generation OPV cells. To that end, the group is targeting the following activities:

- Develop novel ternary systems that can significantly enhance the power conversion efficiency (PCE) values of devices. Systematically survey the structures of third component polymers to establish structure/property relationship on energy level matching, template effects for self-assembly, and the relationship between composition and Voc values.
- Develop new polymers with varied band gaps, energy levels and optimized charge transport behaviors for use as electron donor in OPV solar cells. Detailed structure property relationships are being sought.
- Develop efficient all organic, non-fullerene electron acceptors to replace fullerenes.
- New methods are being developed to create predictive atomistic force fields to fully describe the aromatic semiconducting polymers. These new force fields are being used in conjunction with advanced sampling simulation techniques to predict the structure of OPV polymeric materials in a variety of processing-relevant environments.
- The electronic properties of these polymers are modeled based on sophisticated classical and quantum mechanical calculations in order to understand performance from first-principles considerations.

9.2 Significant Accomplishments in 2015

Ternary Blend Organic Solar Cells **Yu** developed efficient ternary blend OSC with a PCE of 9.2% was developed (Figure 9.2). Their efforts show that the third component can reduce surface trap densities in the ternary blend. Detailed studies unravel that the improved performance results from synergistic effects of enlarged open circuit voltage, suppressed trap-assisted recombination, enhanced light absorption, increased hole extraction, efficient energy transfer and better morphology. The working mechanism and high device performance demonstrate new insights and design guidelines for high performance ternary blend solar cells and suggest that ternary structure is a promising platform to boost the efficiency of OSCs.

Design of Building Blocks for Organic Semiconductor Materials **Marks** developed a new building block, *bithiphenesulfoamide*, as a new photovoltaic materials component. It was designed and developed to offer a strongly electron-withdrawing and strongly dipolar sulfonamide group. This key building blocks allow systematic synthesis of a series of new donor polymers for further exploration of OPV properties.

DFT of Donor Polymers **Galli** and Goldey (UC) used B3LYP density functional techniques to examine the structures and properties of the donor polymers poly-3-oxothieno[3,4-d]isothiazole-1,1-dioxide/ benzo-dithiophene (PID2) and polythieno[3,4-b]-thiophene/ benzodithiophene (PTB7) and the acceptor material [6,6]-phenyl C71 butyric acid methyl ester (PC71BM). Energy levels match experimental cyclic voltammetry data well, with errors of 0.1 eV. The experimental energy levels for these materials reflect the lowest energy geometries that were calculated.

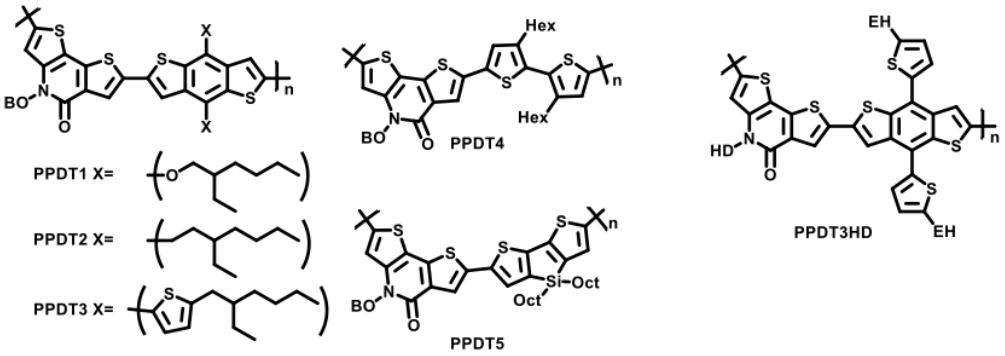


Figure 9.1: Structures of new wide band gap polymers

Molecular Simulations of OPV-revelant Materials **De Pablo** carried out molecular simulation of OPV-relevant materials and investigated the ring stacking behavior of single PTB7 molecules with and without its sidechains, and that of PTB7 in the bulk. It was found that single PTB7 molecules without sidechains show highly coiled configurations with an average 70% of the rings stacked for 50-mers, while steric hindrance in the full PTB7 molecule (with sidechains) reduces this value to 30%. Improved solvation in the a bulk material of PTB7, as compared to PTB7 in the vacuum, increases end-to-end distance by a factor of 3 (for 50-mers) and increases stacking to 70%.

9.3 Research Accomplishments

Development of Novel Photovoltaic Polymers A new series of wide band gap photovoltaic polymers based on the N-alkyl 2-pyridone dithiophene (PDT) unit was developed (Figure 9.1) by **Yu** group. These polymers are effective bulk heterojunction solar cell materials when blended with phenyl-C71-butyric acid methyl ester (PC71BM). They achieve power conversion efficiencies (up to 5.33%), a high values for polymers having such large bandgaps, ca. 2.0 eV (optical) and 2.5 eV (electrochemical). Grazing incidence wide-angle X-ray scattering (GIWAXS) reveals strong correlations between p-p stacking distance and regularity, polymer backbone planarity, optical absorption maximum energy, and photovoltaic efficiency. These polymers exhibit potential as third components in ternary polymer solar cells.

Ternary Blend Organic Solar Cells The integration of multiple materials with complementary absorptions into a single junction device is regarded as an efficient way to enhance the PCE of organic solar cells. However, because of increased complexity with one more component, only limited high-performance ternary systems have been demonstrated previously. An efficient ternary blend OSC with a PCE of 9.2% was developed (Figure 9.2) by **Yu** group. We show that the third component can reduce surface trap densities in the ternary blend. Detailed studies unravel that the improved performance results from synergistic effects of enlarged open circuit voltage, suppressed trap-assisted recombination, enhanced light absorption, increased hole extraction, efficient energy transfer and better morphology. The working mechanism and high device performance demonstrate new insights and design guidelines for high performance ternary blend solar cells and suggest that ternary structure is a promising platform to boost the efficiency of OSCs.

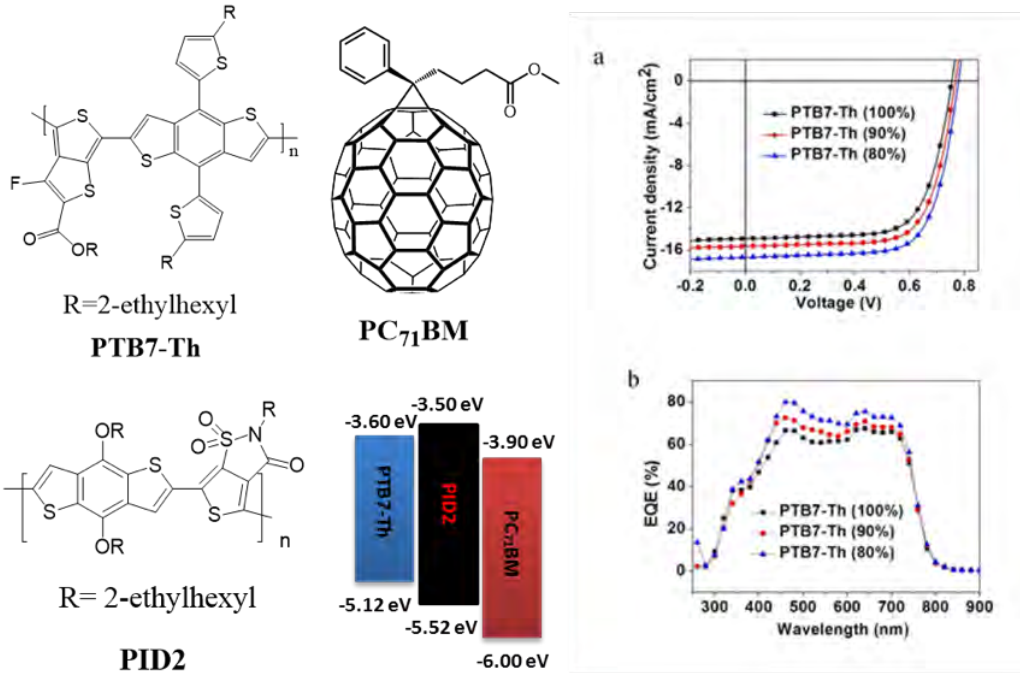


Figure 9.2: Molecular structures of PID2, PTB7-Th and PC71BM, and Energy levels of materials used in the solar cell device. (a) J-V curves of ternary solar cells (PTB7-Th:PID2:PC71BM) with different PTB7-Th:PID2 weight ratios. (b) External quantum efficiencies of ternary solar cells (PTB7-Th:PID2:PC71BM) with different PTB7-Th:PID2 weight ratios.

Design of Building Blocks for Organic Semiconductor Materials *Bithiphenesulfoamide* (BTSA), a new building block for organic semiconducting materials containing a sulfonamide moiety as key functionality, was designed and developed as a new photovoltaic materials component by **Marks** group. This functional group was previously unknown in OPV materials design. An optimized synthesis of BTSA core was achieved during the past year, and provides a very convenient 3-step procedure (Figure 9.3A). The high overall yield, simplicity of the 3-step procedure, and possibilities for upscale production let one to recognize the methodology toward BTSA as one of the shortest and most efficient, including cost-efficiency, synthesis of building blocks for semiconducting materials. It should be noted that the majority of new building block for OPV materials reported now in literature tend to have more and more sophisticated structures undoubtedly defeating the purpose of organic semiconductors to be easy available and cost-efficient. Note, functionalization of BTSA with solubilizing chains and groups required for polymerization also highly efficient and does not require any expensive reagents and catalysts (Figure 9.3B). Molecular material (SM) comprising of BTSA unit flanked with bithiophene groups was synthesized (Figure 9.3C). The study of single crystal structure of SM, first proved the results of DFT calculation used for BTSA design and modeling (see CHiMaD Annual Report 2014) second, revealed important feature of key sulfonamide unit (SO2N) to form a dense network of short contact enhancing intermolecular interaction and affection the packing (Figure 9.3C).

Family of BTSA co-polymers with di- and tri-thiophenes donor units was synthesized and characterized (Figure 9.4). Representative examples of each group are materials FM0183 (BTSA-2T) and FM0318 (BTSA-3T) D-A polymers were synthesized and characterized.

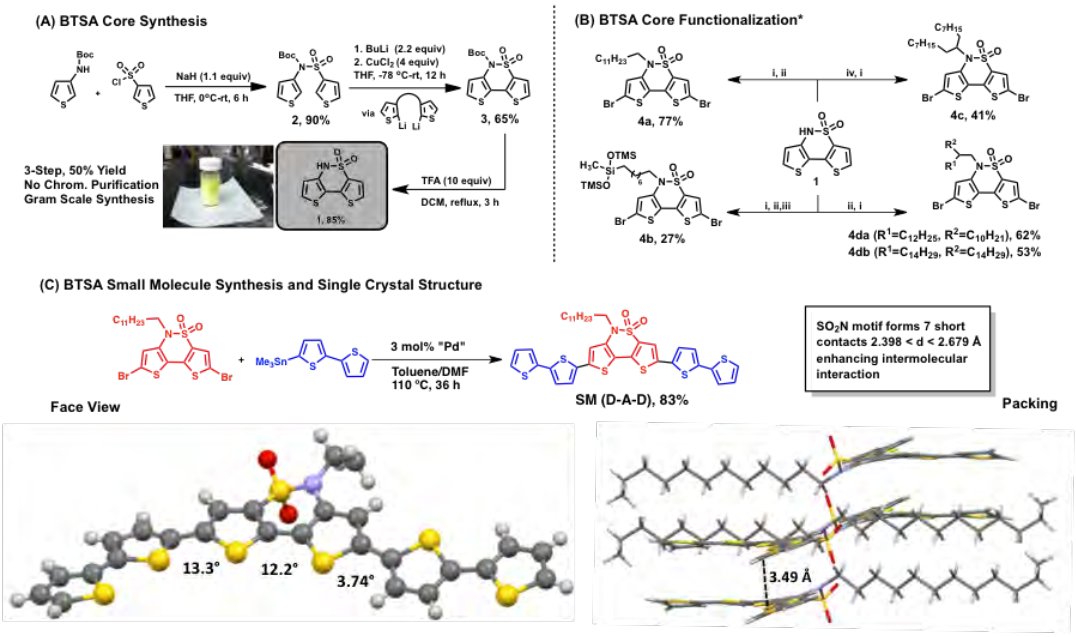
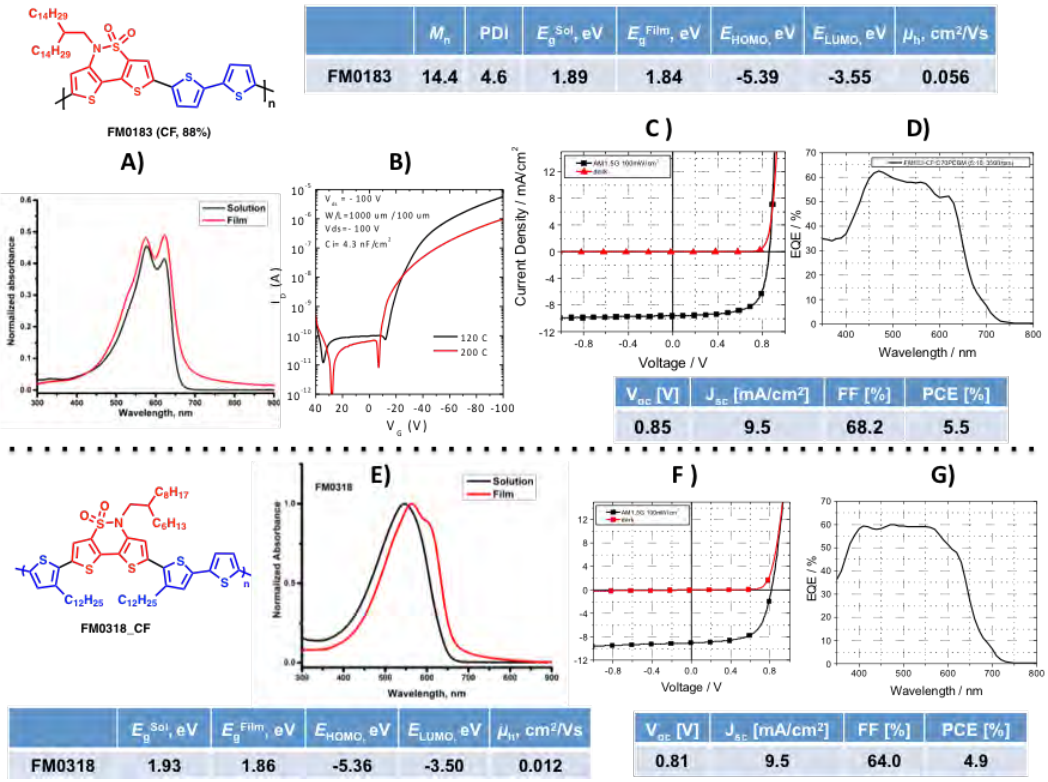


Figure 9.3: (a) Optimized Synthesis and (b) Functionalization of the Bithiophenesulfonamide (BTSA) Core; (c) Synthesis of a BTSA-based Small Molecule (SM) and its Single Crystal Structure

OFETs were fabricated for both materials to study the charge transport. For both material hole mobilities (μ_h) are in the range of highest reported for donor organic materials used in BHJ OPV cells. Interestingly, FM0183 films grown on OTS treated Si/SiO2 substrates demonstrate high crystallinity in film XRD experiments (out-of-plane direction) and have no features in DSC experiments, which is opposite for FM0318. The material has no diffraction peaks in films XRD experiments (out-of-plane) but possess sharp melting and crystallization transitions. OPV cells were fabricated for both polymers using PC71BM as an acceptor. Both materials exhibit high non-optimized PCE clearly indicating the high potential of BTSA unit for further development (Figure 9.4).

Structures and Properties of Donor Material Polymers **Galli** and Goldey (UC) has examined the structures and properties of the donor polymers poly-3-oxothieno[3,4-d]isothiazole-1,1-dioxide/ benzodithiophene (PID2) and polythieno[3,4-b]-thiophene/ benzodithiophene (PTB7) and the acceptor material [6,6]-phenyl C71 butyric acid methyl ester (PC71BM). PTB7 and PID2 are approximated as 1-dimensional periodic systems using plane wave DFT, with two monomers in the unit cell, approximating 2-ethyl hexyl side chains as methyl groups. Energy levels using the B3LYP density functional match experimental cyclic voltammetry values well [Lu, L., et. al.(2014). Nature Photon., 8(9), 716?722], with errors of 0.1 eV, which is visible in Figure 9.5. The groups reported energy levels for these materials reflect the lowest energy geometries which have calculated. The band gaps for dihedral conformers of PTB7 and PID2 are presented in Table 9.1. Backbone twisting for these materials can raise the band gap by 0.5 eV, indicating that local structural order significantly changes electronic structure.

Interfaces Between Donor and Acceptor Material Polymers Pi-stacked interfaces between single donor material polymers and the acceptor material have been computed by **Galli** group using van der Waals-corrected density functionals, which reflect crystalline regions, providing pi-stacking distances of 3.79 Å for PTB7 and 3.95 Å for PID2, which are in



	M_n	PDI	E_g^{Sol}, eV	E_g^{Film}, eV	E_{HOMO}, eV	E_{LUMO}, eV	μ_h, cm²/Vs
FM0183	14.4	4.6	1.89	1.84	-5.39	-3.55	0.056

V_{oc} [V]	J_{sc} [mA/cm²]	FF [%]	PCE [%]
0.85	9.5	68.2	5.5

	E_g^{Sol}, eV	E_g^{Film}, eV	E_{HOMO}, eV	E_{LUMO}, eV	μ_h, cm²/Vs
FM0318	1.93	1.86	-5.36	-3.50	0.012

V_{oc} [V]	J_{sc} [mA/cm²]	FF [%]	PCE [%]
0.81	9.5	64.0	4.9

Figure 9.4: BTSA-2T polymer (FM0183): (a) Optical Absorption; (b) OFET Transfer characteristics; (c) and D J-V Curve and EQE spectrum. BTSA-3T polymer (FM0318): (e) Optical absorption; (f) and (g) J-V Curve and EQE spectrum

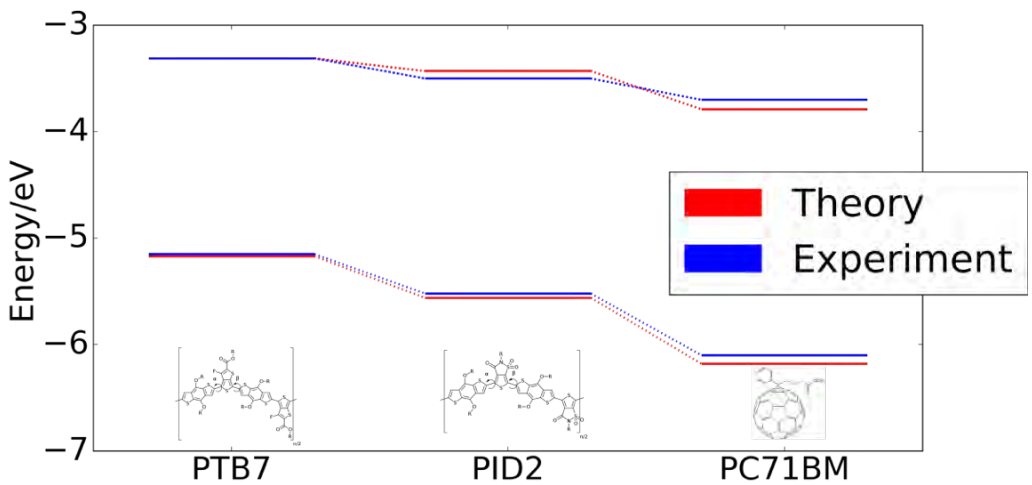


Figure 9.5: Energy levels (eV) for three organic photovoltaic materials from experiment [Lu, L., et. al.(2014). Nature Photon., 8(9), 716-722] and theory (periodic plane-wave B3LYP).

PTB7 Conformer	α_1	α_2	β_1	β_2	E_g@B3LYP (ev)
cis-trans	54	54	133	133	2.29
cis-cis	21	22	26	20	1.81
trans-cis	136	114	41	72	2.32
trans-trans	152	153	158	150	1.82
PID2 Conformer	α_1	α_2	β_1	β_2	E_g@B3LYP (ev)
cis-trans	47	44	137	139	2.27
cis-cis	9	10	14	14	1.93
trans-cis	138	118	40	70	2.42
trans-trans	154	157	158	150	2.05

Table 9.1: Backbone sulfur-sulfur dihedrals (in degrees) and B3LYP band gaps (eV) for PTB7 and PID2 donor polymers. The cis-cis conformer was calculated to be the ground state configuration for both materials.

good agreement with experimental pi-pi spacings from grazing incidence wide-angle x-ray scattering values (3.79 Å for PTB7) [Szarko, J. M., et. al (2010). Adv. Mater., 22(48), 5468-5472]. Since experimental structures are largely amorphous, characterization of structural disorder must be performed using statistical sampling of molecular dynamics trajectories. Our use-case group collaborators, Reid (UC) and **de Pablo**, have provided us with several such trajectories (300K, NPT, 200 snapshots, spaced 1000 femtoseconds apart), with which we have assessed the effect of twisting, bending, and stacking of these polymer chains on the frontier molecular orbital energies (using the PBE density functional), which is visible in Figure 9.6. Side-chain and backbone twisting broaden computed energy levels with standard deviations of 0.2 eV. The inter-chain hole transfer matrix elements, shown in Figure 9.6 in the inset, have been computed from the frontier molecular orbitals of the stacked chain configurations.

Molecular Simulation of OPV-relevant Materials Molecular simulation of OPV-relevant materials presents significant challenges compared to that of many non-crystalline polymer systems. To assess charge transfer and overall device efficiency, details of both pi-pi stacking between polymers at small scales, and the arrangement of polymers and fullerenes at large scales is required. While traditional atomistic simulations provide the high resolution needed to assess nano-scale properties, they cannot easily approach the time and length scales relevant to overall film morphology and performance. The **de Pablo** group thus addressed the problem of simulating OPVs from two fronts: atomistic simulations to capture molecule-level arrangement, and highly coarse-grained simulations to model larger scale morphologies. Once a coarse-grained morphology is generated, a detailed atomistic representation can be grown in, allowing investigation of large-scale experimentally relevant configurations.

To generate atom-level configurations, an accurate force field is essential. However, standard force fields such as OPLS (Optimized Potentials for Liquid Simulations) do not describe the highly conjugated molecules used in OPV. We thus combine electronic structure calculations with relevant OPLS parameters to generate a new force field which can accurately describe OPV materials. We focus our efforts on simulating PTB7 and PCBM71, as a starting point for investigating more complex materials. Frequency analysis of PTB7 shows low frequency modes exist only between rings of the conjugated polymer, and high frequency modes (relevant only at extremely high temperatures) exist only within

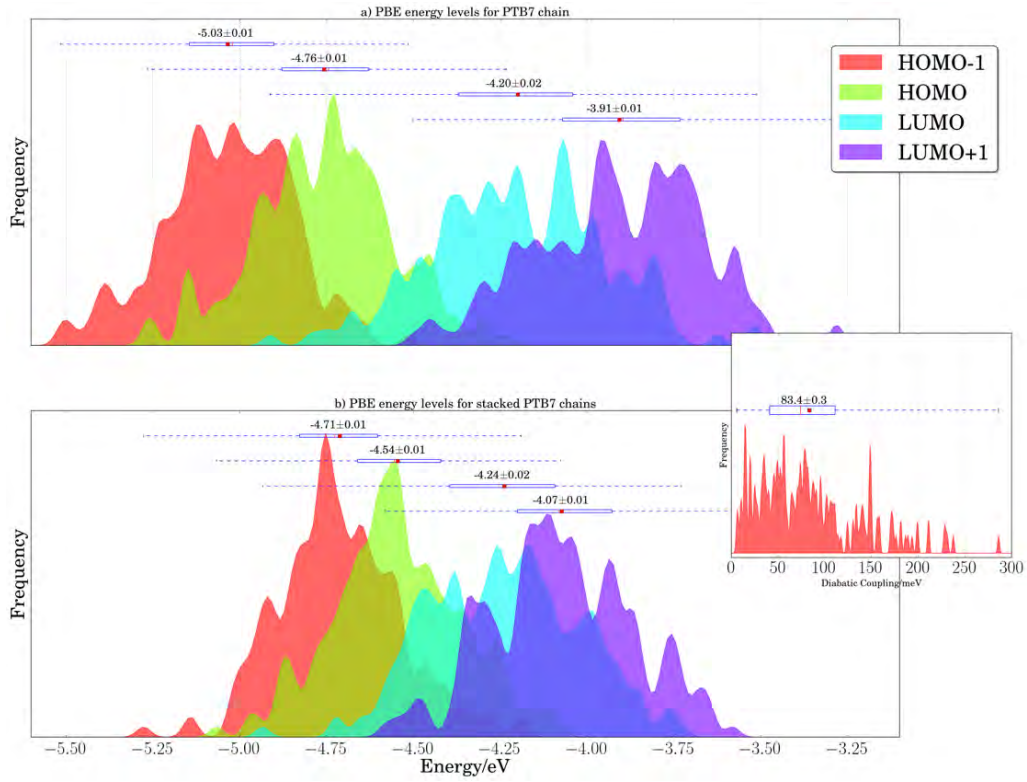


Figure 9.6: Computed PBE energy levels (in eV) for structures from molecular dynamics simulations of PTB7, using one chain (a) and two chains (b). Box plots indicate the middle two quartiles for the data, and average band positions with standard deviations of the mean are present above the relevant box plot. Hole transfer inter-chain coupling elements (in meV) for the pi-pi stacked PTB7 chains are presented in the inset graph.

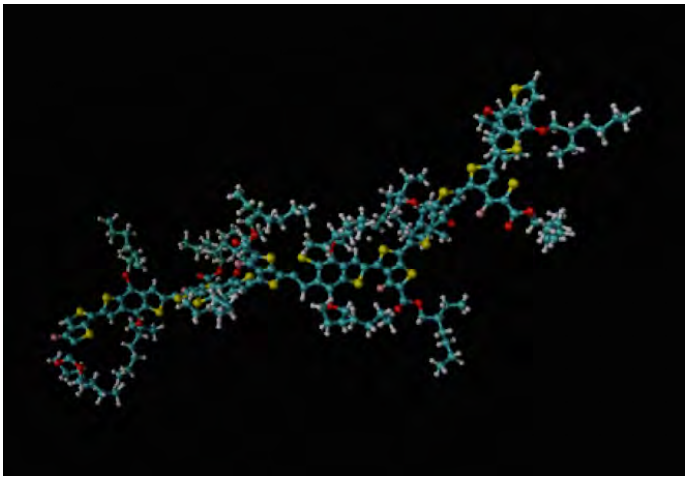


Figure 9.7: Configuration of a single PTB7 molecule in vacuum. When equilibrated, these molecules show varying degrees of ring stacking based on their length, and steric hindrance due to sidechains.

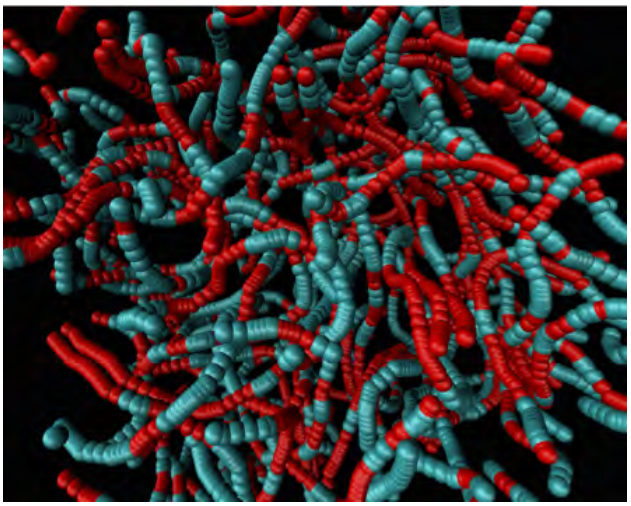


Figure 9.8: Bulk PTB7 configuration. Polymers are represented as bead-chains, with stacked beads colored red. As can be seen, a fair degree of ring stacking exists, with much of it being between different chains.

the rings. Thus, the rings of the PTB7 are held rigid, while parameters corresponding to torsion and bending between rings are parameterized using B3LYP/6-311++g method and basis set. We find out-of-plane bending to be 15 times more stiff than torsion between the rings, leading to a high persistence length. A similar parameterization process is followed for PCBM71, where known parameters are taken from OPLS, high frequency modes are held stiff, and low frequency modes are parameterized using electronic structure techniques.

To verify the accuracy of this force field, we investigate the density, glass transition, and resulting morphology of materials produced using the newly-constructed PTB7 and PCBM71 force fields. Experimental values of the glass transition temperature for PTB7 range between 55 and 95°C. We find a glass transition temperature of 65°C. Experimental density of PTB7 is estimated at 1.24 g/cm^3. We report two densities. In a perfectly ring-stacked configuration, our model of PTB7 shows a density of 1.28 g/cm^3, while a bulk simulation of PTB7 cooled from a melt over 5 nanoseconds shows a density of 1.11 g/cm^3. Experimental films are formed over the course of minutes, so lower densities in simulated films are expected.

While charge can transport fast along a polymer chain, inter-chain charge transport is necessary in order to reach the appropriate electrode. **De Pablo** investigated the ring stacking behavior of single PTB7 molecules with and without its sidechains, and that of PTB7 in the bulk. Single PTB7 molecules without sidechains show highly coiled configurations with on average 70% of the rings stacked for 50-mers (Shown in Figure 9.8), while steric hindrance in the full PTB7 molecule (with sidechains) reduces this value to 30%. Moving to stacking in the a bulk material of PTB7, we find that improved solvation, as compared to PTB7 in the vacuum, increases end-to-end distance by a factor of 3 (for 50-mers) and increases stacking to 70%. For efficient charge transfer, polymers must stack with other polymers, not only themselves. We find that in the bulk material, 40% of stacking is with other chains, while 60% of stacking interactions are with itself (Figure **??**).

9.4 Collaborations

9.4.1 CHiMaD Collaborations

MD force field generation for Organic Bulk Heterojunction Polymer Solar Cells
*Guilia **Galli** (UC), Juan **de Pablo** (UC)*
The collaboration between **Galli** and **de Pablo** groups has focused on the generation and validation of an atomistic force field for simulations of the donor polymer PTB7. Several potential energy surfaces for calibration of internal coordinate parameters were calculated. **Galli** group has also used trajectories with this force field to statistically sample geometries for their electronic structure calculations.

Polymer Solar Cells
*Monica **Olvera de la Cruz** (NU), Tobin **Marks** (NU)*
Through this collaboration, **Olvera** and **Marks** groups are developing new design principles for electron accepting polymers and to establish the structure/property relationship of these n-types of organic polymers for the purposes of solar energy conversion and organic electronic applications. The goal of this work is to generate new materials that will exhibit a greater potential than existing fullerene derivatives as n-type semiconducting materials.

Data Mining for Design and Development of OPV Materials
*Luping **Yu** (UC), Guilia **Galli** (UC), Ankit **Agrawal** (NU), Alok **Choudhary** (NU), Christopher **Wolverton** (NU)*
During the *CHiMaD Materials Design Workshop I* use-case presentation by Goldey (UC) and Schneider (UC), a possible collaboration between the Organic Bulk Heterojunction Polymer Solar Cells and Data Mining use-case groups came to light. After initial discussions between use-case groups including Goldey (UC), Schneider (UC), Ward (NU), Furmanchuk (NU), Paul (NU), it was decided that there is little correlation between device efficiency and energy levels of polymeric material, but stronger correlations between power conversion efficiency and morphology-dominated properties.The groups will be exploring the possibility of using data mining for determining the uncontrolled morphology of active layer in order to support building of OPV devices.

9.4.2 NIST Collaborations

Energy Level Validation for Organic Bulk Heterojunction Polymer Solar Cells
*Guilia **Galli** (UC), Luping **Yu** (UC), Lee Richter (NIST)*
This collaboration involved the measurement of ultraviolet photoelectron spectroscopy values for donor and acceptor material ionization potentials and electron affinities. **Yu** group has provided the materials, and Richter (NIST) and his experimental colleagues at NIST are measuring the glass transition temperature, UPS for determining HOMO/LUMO energy levels and the origin of Voc/composition correlation in ternary solar cells levels to validate the theoretical best estimates of material energy levels generate by the **Galli** group.

New Atomistic and Coarse-Grained Models
*Juan **de Pablo** (UC), Luping **Yu** (UC), Tobin **Marks** (NU), Giulia **Galli** (UC), Lee Richter (NIST)*
In collaboration with **Yu**, **Marks**, **Galli** and Richter (NIST), the **de Pablo** group has developed new atomistic models and coarse-grained models for description of OPV materials. The results of these efforts were presented at a workshop organized in November at the

University of Chicago that involved several leading OPV researchers from around the world, including three participants from NIST.

9.4.3 External Collaborations

GWIXS of Ternary OPV Systems

*Luping **Yu** (UC), Wei Chen (Argonne National Laboratory)*

This collaboration with Chen group at ANL involves the experimental efforts regrading Grazing incidence wide-angle X-ray scattering (GWIXS) measurements of OPV systems this use-case is working on.

Ultrafast Spectroscopy

*Luping **Yu** (UC), Lin Chen (Argonne National Laboratory/ Northwestern University)*

This collaboration with Chen group at ANL involves the experimental efforts regrading ultrafast spectroscopy measurements of OPV systems this use-case is working on.

9.5 Publications and Presentations

8 Number of CHiMaD-supported publications in 2015 by Organic Bulk Heterojunction Polymer Solar Cells use-case group. Please see chapter 20 for details. [3, 6, 7, 8, 28, 29, 30, 31]

13 Number of presentations on CHiMaD supported research in 2015, please see section 21.8 for the complete list.

1 Organic Bulk Heterojunction Polymer Solar Cells use-case group organized an international symposium entitled *Advances and Challenges in Soft Matter Photovoltaic Research* held at Institute of Molecular Engineering, University of Chicago on November 13-14, 2015.

9.6 CHiMaD Team

Organic Bulk Heterojunction Polymer Solar Cells Use-Case Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Luping Yu	Principal Investigator	UC/CHEM	
Juan de Pablo	Principal Investigator	UC/IME	
Guilia Galli	Principal Investigator	UC/IME	
Tobin Marks	Principal Investigator	NU/MSE	
Matthew Goldey	Postdoctoral Researcher	UC/IME	Organic bulk heterojunction polymer solar cells *(Galli)*
Daniel Reid	Graduate Student	UC/IME	Simulation of OPV materials *(de Pablo)*
Alexander Schneider	Graduate Student	UC/CHEM	Organic bulk heterojunction polymer solar cells *(Yu)*
Luyao Lu	Graduate Student	UC/CHEM	Novel materials for OPV applications *(Yu)*

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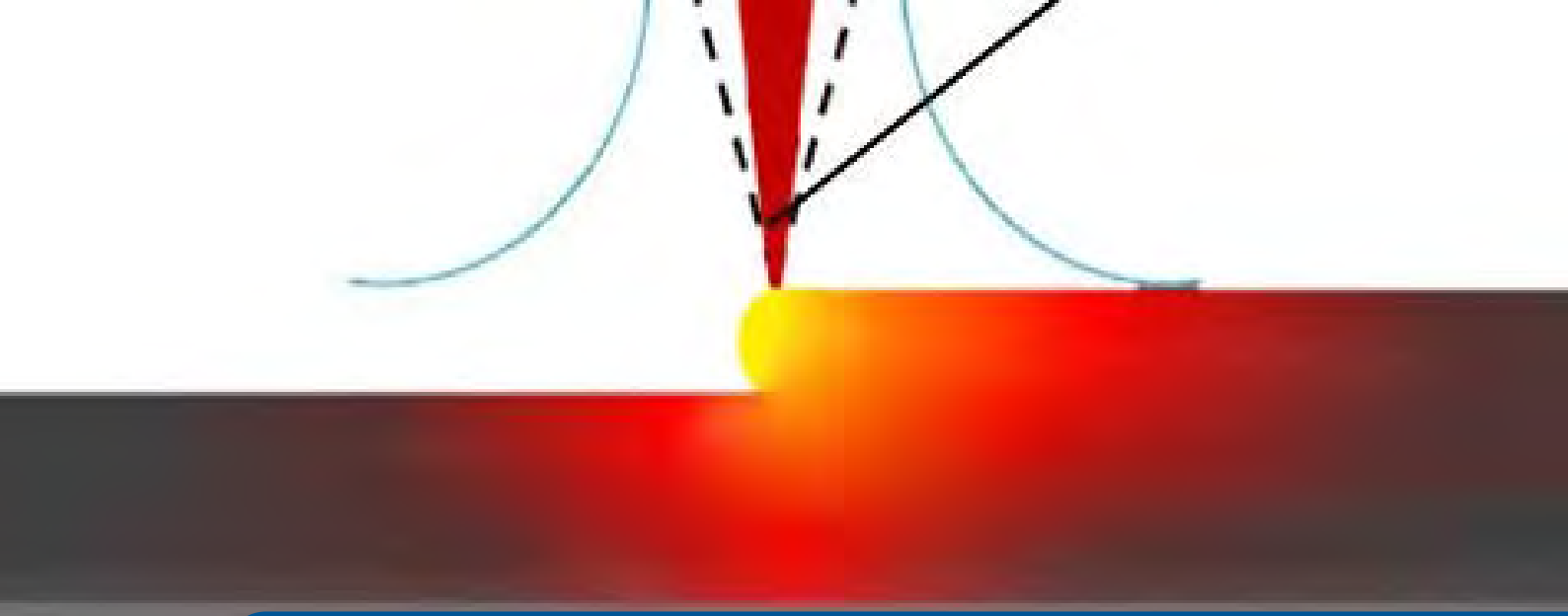


10. Additive Manufacturing

Jian Cao (NU)

10.1 *Significance & Research*

Additive manufacturing breaks three fundamental manufacturing tradeoffs: capital versus scale, capital versus scope, and capital verses complexity. It also significantly reduces material waste by placing materials only where needed. Widespread acceptance of additive manufacturing will increase supply chain efficiency, reduce time to market, move from mass production to mass customization, and sustain the environment. This will spur a technology renaissance by bridging manufacturing of all scales with material design and will broaden participation by disseminating accessibility to cutting-edge manufacturing processes.

Powder flow is a critical element in controlling the quality of parts made by powder deposition process, one additive manufacturing process. Rapid on/off powder control has been achieved, which has virtually eliminated the material transport delay by reducing it from 24.8 seconds to 0.20 seconds. This control system allows powder start and shutoff strategically under the control to reduce the waste of both powder and machine time. Additionally, it reduces the inadvertent adhesion of loose powder to the component. More interestingly, the precise powder control also allows for rapid toggling between materials in multi-material builds.

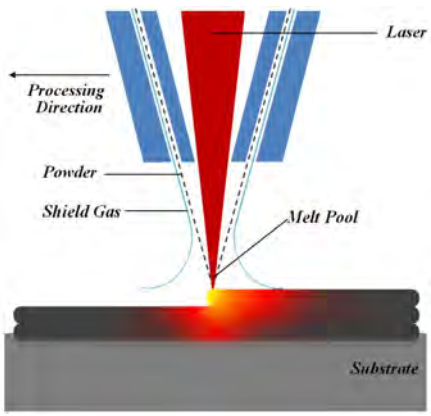


Figure 10.1: Laser Deposition

The next step in powder control, with the ultimate goal of creating an integrated multi-parameter control of laser powder deposition processes to explore the material design freedom and capability, is to enable analog metering control so that the powder deposited per unit length may be maintained uniformly. The metering solution will require the design and manufacture of a custom valve. Once the metering hardware system is online, the system

variables can be experimentally determined and the controller can be tuned. The powder control system will then be implemented and its performance will be evaluated.

10.2 Collaborations

10.2.1 CHiMaD Collaborations

Additive Manufacturing of Co-Alloys
*Jian **Cao** (NU), Gregory **Olson** (NU), Wing-Kam **Liu** (NU)*
The graduate students from the three groups are working in collaboration on the topic of additive manufacturing.

10.2.2 NIST Collaborations

Additive Manufacturing
*Jian **Cao** (NU), Wing-Kam **Liu** (NU), Gregory **Olson** (NU), Lyle Levine (NIST), Li Ma (NIST), Carelyn Campbell (NIST), Mark Stoudt (NIST)*
There is an active communication and exchange of research findings between these groups.

10.2.3 External Collaborations

Collaboration with DMG-MORI USA
*Jian **Cao** (NU)*
An industrial collaboration on machine control has been established with DMG-MORI, USA, worth over $1B.

10.3 Publications and Presentations

4 Number of CHiMaD-supported publications in 2015 by Additive Manufacturing seed group. Please see chapter 20 for details. [21, 22, 23, 24]

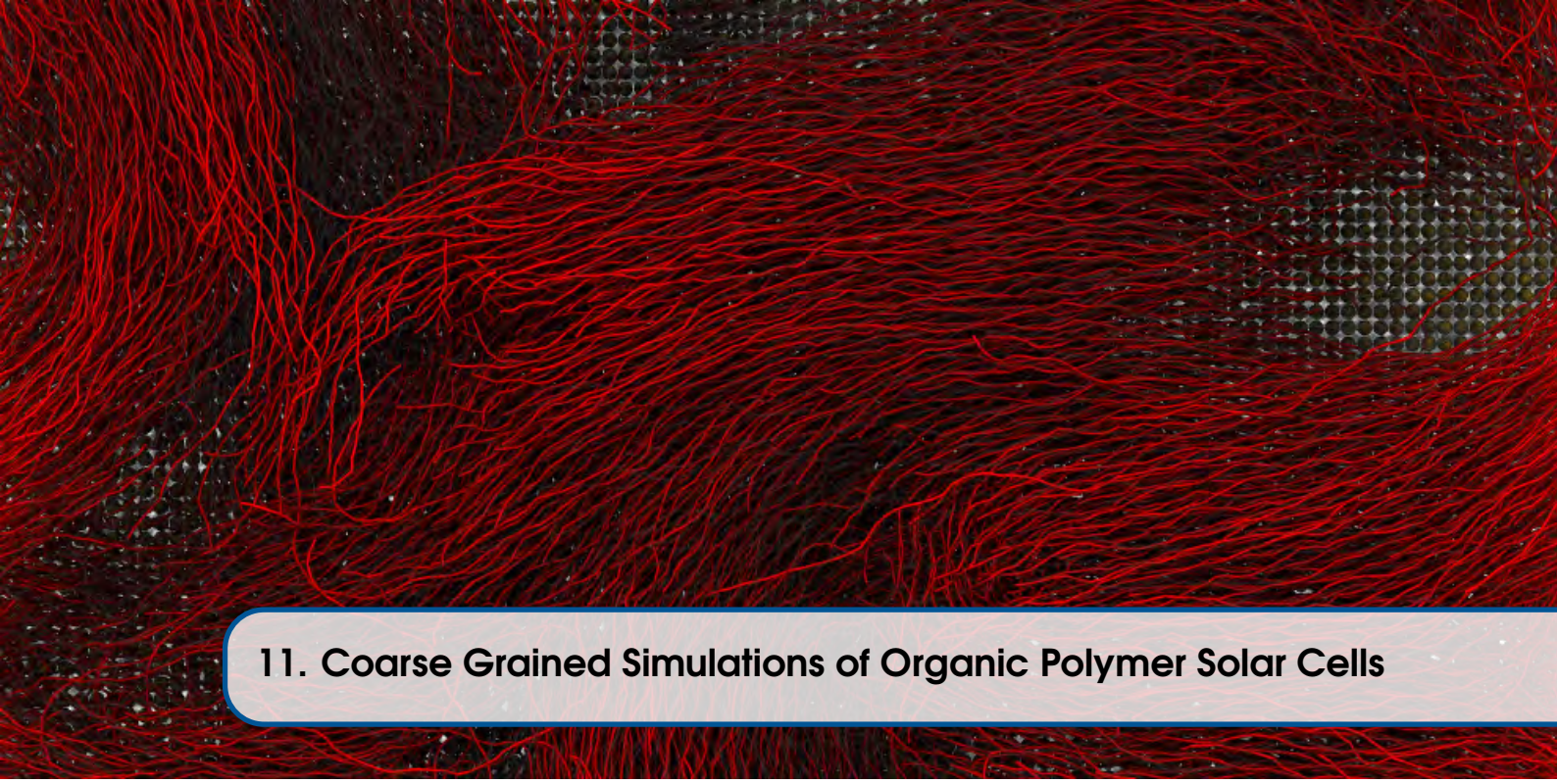
2 Number of presentations on CHiMaD supported research in 2015, please see section 21.10 for the complete list.

2 Additive Manufacturing seed group has worked with Campbell (NIST) to co-fund the National Academy of Sciences workshop entitled *Predictive Theoretical and Computational Approaches for Additive Manufacturin* held at Washington D.C. on October 7-9, 2015; presentation slides and additonal videos are available at
$http://sites.nationalacademies.org/PGA/biso/IUTAM/PGA_{1}68737$.

Cao also organized the *Roadmapping for Innovation in Sheet Metal Forming Workshop* on May 4, 2015.

10.4 CHiMaD Team

Additive Manufacturing Seed Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Jian Cao	Principal Investigator	NU/ME	
Jennifer Bennett	Graduate Student	NU/ME	Flow Control in Additive Manufacturing to Enable Building Functionally Graded Materials *(Cao, Ehmann (NU))*



11. Coarse Grained Simulations of Organic Polymer Solar Cells

Monica Olvera de la Cruz (NU)

11.1 *Significance & Research*

Investigating polymer-polymer blend film morphology via coarse-grained simulations provides a different and complementary perspective to experrimentation, for better understanding of the physical processes that occur during blend film formation.

De la Cruz group performed coarse grained simulations of wormlike chains to elucidate the influence of number-average molecular weight (M_n) on the blend film morphology and photovoltaic performance of all-polymer solar cells fabricated with the donor polymer PTPD3T and acceptor polymer N2200 (see Publication [32]). The simulations showed that the M_n variation of both PTPD3T and N2200 polymers greatly influences both intrachain and interchain correlations, the degree of phase separation and morphology of the blend. The experimental study showed that increasing M_n for both polymers shrinks blend film domain sizes and enhances donor-acceptor polymer-polymer interfacial areas, which leads to an increase in short-circuit current densities (J_{sc}). However, when M_n increases the degree of chain entanglement increases, which promotes charge trapping in intramolecular charge transport, reducing cell fill factors (FF). Therefore, there is an optimized M_n for well-balanced exciton dissociation and charge transport characteristics, which involves increasing both polymers M_n such that they both have very close values of M_n.

The TEM morphologies are in agreement with the simulations results, summarized in Figure 1. The lowest M_n of both polymers is strongly phase-separated with large fibril-like polymer microstructures. Such morphologies are known to introduce large grain boundaries with poorly connected polymer networks, suppressing charge carrier transport. For medium M_n of both polymers the film morphologies begin to show more intermixed features, which would enable more efficient exciton scission. This is accompanied by relatively continuous polymer domains, which can be critical for efficient charge transport. Finally, for the highest M_n polymers, the blend films display highly disordered characteristics, with the least degree of semi-crystalline polymer domains.

Investigating polymer-polymer blend film morphology via simulations provides a different and complementary perspective, for better understanding of the physical processes that occur during blend film formation. Considering that the phase separation feature sizes are a few tens of nm, which is prohibitively large in full atomistic simulations, large-scale molecular dynamics (MD) simulations were employed on a general coarse-grained model of blends of the two polymers. This model provides an excellent platform to analyze the morphological characteristics of the polymer-polymer blends. In this model, each monomer unit is coarse-grained into a single bead of size σ, connected via a bond potential, $U_{bond}(r) = \frac{1}{2}k_{bond}(r-r_0)^2$, and an angle potential, $U_{angle}(\theta) = \frac{1}{2}k_{angle}(\theta-\pi)^2$, to a nearby monomer unit. The bond rest length r_0 is arbitrarily set at 0.84σ to avoid bond crossings. Interactions for non-bonded beads are modeled by a shifted Lennard-Jones potential, which is written as $U_{LJ}(r_{ij}) = 4\varepsilon[(\frac{\sigma}{r_{ij}})^{12} - \frac{\sigma}{(}r_{ij})^6)] - U_{LJ}(r_{cut})$ for $r \leq r_{cut}$ ($r_{cut} = 3.0\sigma$) and $U_{LJ}(r_{ij})$ for $r > r_{cut}$. $\sigma \approx 1.6$ nm specifies the unit of length, and the Lennard-Jones potential wells for the description of monomer interactions are $\varepsilon_{AA} = 0.5\varepsilon_0$; $\varepsilon_{AB} = 0.3\varepsilon_0$; $\varepsilon_{BB} = 0.1\varepsilon_0$, where $\varepsilon_0 \approx 0.38$ kcal mol^{-1} represents the unit of energy in our simulations. The condition of $\varepsilon_{BB} < \varepsilon_{AB}$ is used as $\varepsilon_{BB} > \varepsilon_{AB}$ will drive the polymer blend to phase separate instead of phase separation. Constraints in $k_{bond} = 330\varepsilon_0$ and $k_{angle} = 20\varepsilon_0$ describe reasonable rigidity for such worm-like chains. An extra layer of fixed beads acting as a boundary condition for the bottom of the simulation box is included to model the film substrate. The model presented here can provide general insights into OPV polymer selection beyond the specific n- and p-type polymers employed in this work.

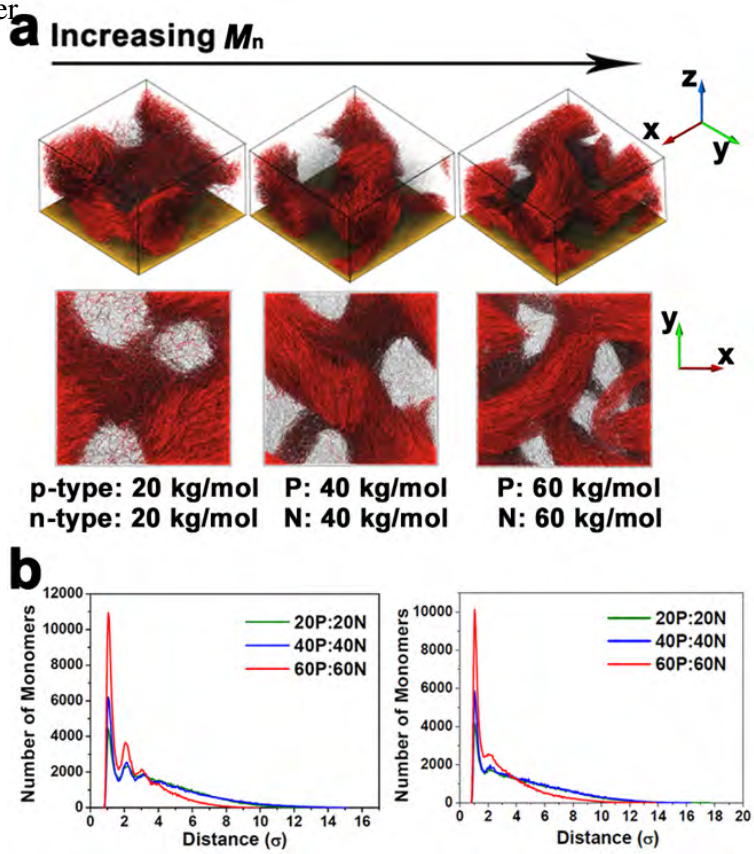


Figure 11.1: MD simulations of all-polymer blend morphology. a) Polymer-polymer blend film morphology from coarse-grained MD simulations. The n-type polymer is represented by red beads and p-type polymer is by grey beads. b) Left (right): Number of monomers of p- (n-) type at a certain distance from monomer of n- (p-) type averaged among all monomers of p- (n-) type. The distance between a monomer of p- (n-) type to its nearest neighboring monomer of type n- (p-) is measured.

11.2 Collaborations

11.2.1 CHiMaD Collaborations

Polymer Solar Cells

*Monica **Olvera de la Cruz** (NU), Tobin **Marks** (NU)*

Through this collaboration, **Olvera** and **Marks** groups are developing new design principles for electron accepting polymers and to establish the structure/property relationship of these n-types of organic polymers for the purposes of solar energy conversion and organic electronic applications. The goal of this work is to generate new materials that will exhibit a greater potential than existing fullerene derivatives as n-type semiconducting materials.

11.3 Publications

1 Number of CHiMaD-supported publications in 2015 by Coarse-grained simulations of Organic Polymer Solar Cells seed group. Please see chapter 20 for details. [32]

5 Number of presentations on CHiMaD supported research in 2015, please see section 21.11 for the complete list.

11.4 CHiMaD Team

Coarse Grained Simulations of Organic Polymer Solar Cells Seed Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Olvera de la Cruz	Principal Investigator	NU/MSE	
Victor Pryamitsyn	Postdoctoral Researcher	NU/MSE	*(Olvera)*

12. Impact Mitigation

Heinrich Jaeger (UC), Sid Nagel (UC), Juan de Pablo (UC)

12.1 *Significance & Research*

The damaging effects of blunt impact on human physiology and health have been most notable in the manifestation of the high rates of chronic traumatic encephalopathy (CTE) in athletes, particularly football players. While this is the focus of current sports injury prevention, impacts to soft tissues are the basis for many chronic joint and musculoskeletal diseases. In team sports athletes rely on pads of geometrically structured, non-linear, time-dependent polymeric materials (e.g. elastomers, foams, thermoplastics, gas bladders, etc.), to absorb energy, limit momentum transfer, and reduce force at velocities that can exceed 45 m/s and energies up to 75 J. In many cases such materials are clearly inadequate, and there is a pressing need to reduce impact injuries to the head and body from a wide variety of threats in sporting, industrial, and military applications. Advances in protective materials have been incremental due to a lack of dynamic material property data and a lack of predictive models to spur innovation. The design goals of this Seed group are to develop innovative materials for impact mitigation that will be superior to those available today, and to do so by relying on predictive models coupled to high-precision experimentation in the context of both liquid and solid shock absorbing systems.

Several critical needs that currently limit progress are being addressed in this work:

Novel Metrologies for Multiaxial Impact with Distributed Force Measurements Coupled to Measures of the Time-evolving Volumetric Strain Fields Inside And On The Surface of a Material As It is Loaded At High Rates. **Jaeger** group has developed the capability to measure such fields in colloidal suspensions that can absorb impact at ultrafast rates. Figure 12.1 shows a representative measurement of the strain, measured using ultrasound techniques at frame rates of 10,000 per second, as it propagates through a starch suspension immediately after a blunt impact. Moving forward, **de Pablo** and **Jaeger** groups will develop multiscale modeling techniques based on concepts from Stokesian dynamics, friction dynamics, and jamming, that will be used to interpret experimental data, to identify key design principles, and to optimize materials for specific applications.

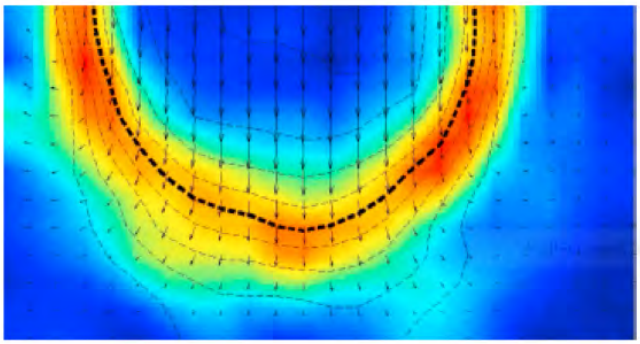


Figure 12.1: Ultrasonic measurement of strain inside dense, opaque suspensions of starch, shortly after blunt impact. Images taken at 10,000 frames per second (Jaeger group).

Development of Innovative Materials Strategies By identifying regions of a material that exhibit high or low local shear and bulk modulus, the **Nagel** group can selectively eliminate (or prune) such regions in order to arrive at systems that exhibit auxetic behavior and that are capable of dissipating strain in controlled directions. Such materials are currently being designed by **de Pablo** and **Nagel** groups by relying on computer models that identify weak or strong regions in the context of jammed particulate samples. Figure 12.2 shows an example of a macroscopic two dimensional material that was designed on the computer and subsequently prepared by laser cutting. The material exhibits a negative Poisson ratio, and the predicted deformation agrees quantitatively with that observed in experiments. Moving forward, a new computational platform, based on concepts from artificial evolution, will enable material discovery of novel architectures and faster material optimization, in two and three dimensions.

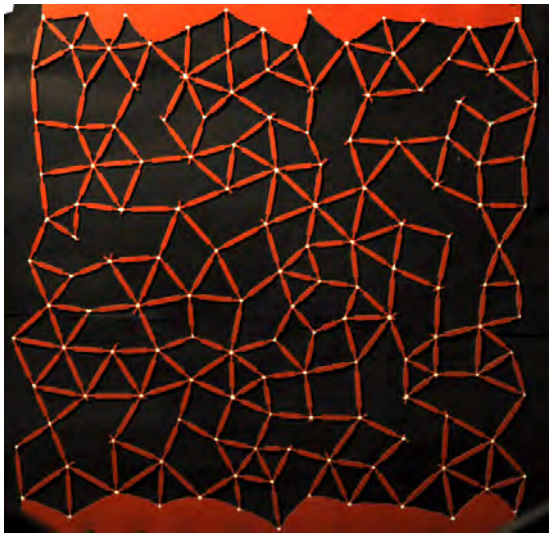


Figure 12.2: Ultrasonic measurement of strain inside dense, opaque suspensions of starch, shortly after blunt impact. Images taken at 10,000 frames per second (Jaeger group).

The successful execution of this proposal will provide scientists with the capabilities to exploit truly innovative concepts in energy dissipation such as force deflection and interface slip to further increase performance and tailor materials and architectures for the impact frequencies and energies that represent the highest risk for injury.

12.2 Collaborations

12.2.1 NIST Collaborations

Development of Novel Metrologies

*Juan **de Pablo** (UC), Sid **Nagel** (UC), Heinrich **Jaeger** (UC), Chealsea Davis (NIST), Aaron Foster (NIST)*

The efforts of this seed group complement those at NIST by Foster (NIST) and Davis (NIST), who are developing metrologies for multiaxial dynamic loading coupled with distributed force measurement, and volumetric exterior strain measurements. Both institutes have expertise in materials for energy dissipation. A collaborative visit by Foster (NIST) and Davis (NIST) to Chicago in February of 2016 was used to identify specific targets for the immediate future collaborations that will involve joint experiments, as well as exchange of students and senior personnel between CHiMaD and NIST.

12.3 CHiMaD Team

Impact Mitigation Seed Group Researchers		
Name	**Position**	**Affiliation**
Juan de Pablo	Principal Investigator	UC/IME
Sid Nagel	Principal Investigator	UC/PHY
Heinrich Jaeger	Principal Investigator	UC/PHY

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13. Materials Data Facility

Ian Foster (UC)

Significance

Materials innovation has been a critical component and driver of economic prosperity and competitiveness for millennia. Yet, the process by which new materials are designed, developed, manufactured, and deployed remains incredibly slow and inefficient. With the Materials Data Facility (MDF), we aim to develop and deploy a set of flexible services that will support modern materials research by allowing researchers to publish and discover datasets regardless of size and from a variety of data storage endpoints. The MDF services will allow users to publish, share, discover, access, and obtain data from past experiments and simulations and facilitate data exchange mechanisms to help prevent redundant work, to encourage broader data synthesis where appropriate, and to begin building the data infrastructure necessary to realize in silico materials discovery. In a cross-disciplinary center, such as CHiMaD, data sharing and data availability (e.g. between computational researchers and experimental researchers) will play a key role in driving effective and impactful collaboration. Beyond the immediate benefits to CHiMaD, MDF will play a role in ensuring that the scientific results from CHiMaD are made widely available to the community for years to come. We also see opportunities to partner with researchers at NIST to improve the discoverability and availability of a variety of reference datasets of particular interest to the materials research community.

13.1 Design Goals

The Materials Data Facility will investigate next generation materials database and data sharing techniques to support the MGI and NIST goals, and deploy and operate cloud-hosted services and other data resources to support CHiMaD collaborations and the materials science research community more broadly. The initial MDF Year 1 focus is on data publication, with an emphasis on building the necessary web interfaces and APIs to support researcher self-service data publication from a variety of data storage endpoints (e.g. institutional storage, laboratory data servers, Amazon S3 cloud resources, etc.) to

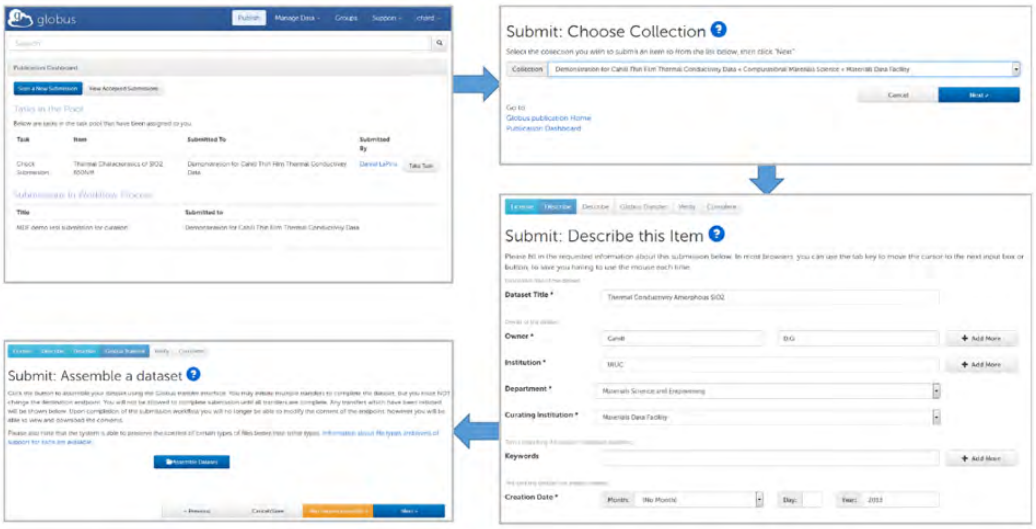


Figure 13.1: Dataset submission workflow in MDF. (clockwise from the upper left) Creating a new submission, choosing a collection to add the submission to, describing the item with customizable metadata fields, and assembling the underlying dataset

simplify data sharing, archiving, and description of datasets to increase transparency and encourage data reuse. Additionally, we are operating a storage allocation at NCSA to begin ingesting datasets in early 2016, and we are developing the required infrastructure and tools to allow indexing and deep discovery of distributed scientific datasets via centralized search.

13.2 Materials Data Facility

The Materials Data Facility is a set of services designed to simplify the process by which materials science researchers publish, discover, share, and reuse datasets. The primary focus of the first phase of the MDF project is the deployment, operation, and iterative improvement of a data publication service, provided as a centralized service to reduce cost to operate, and to reduce friction to drive adoption by institutions and researchers. With MDF, users will be able to publish and discover data via a web user interface (UI) or programmatically via associated REST interfaces (in development). User identity, user group management, and data transfer have been integrated with existing production-level services already provided by Globus [Foster, IEEE Internet Computing 3 (2011): 70-73]. Collections within MDF contain logically similar datasets, and allow for configurable workflows, metadata forms, storage endpoints, dataset unique identifiers, and other collection-specific policies. Datasets within collections are described by the prescribed collection-specific metadata schema, and have an associated data endpoint where raw and derived data are stored. Importantly, while initial storage for the MDF pilot has been allocated at NCSA (UIUC), the data endpoints can be at any location capable of hosting a Globus endpoint: i.e. locally-hosted storage, repository-specific storage, institutional storage, or even cloud storage on Amazon S3. After a dataset is assembled, the associated metadata is indexed to facilitate materials dataset discovery.

13.2.1 Publishing and Discovering Data with MDF

As of December 2015, we have deployed a production data publication service and allocated 100TB of reliable networked storage at National Center for Supercomputing Applications (NCSA) to support our initial users. We are now in the process of identifying key datasets, particularly those associated with CHiMaD researchers, to demonstrate the end-to-end data publication flow. Efforts are ongoing to develop metadata schemas and controlled vocabularies, in conjunction with researchers at NIST, to describe materials resources at a general level (e.g. experimental technique, material type, material morphology, etc.). We are also working to improve MDF metadata schema creation interfaces, one of the remaining challenges before the publication process can be considered self service.

Data published with the MDF data publication service is able to be identified (e.g. associated with a persistent DOI or Handle); described with custom metadata; and curated via custom workflows. These datasets are made accessible via Globus (to handle large datasets) and via HTTP (in development for smaller datasets), searchable via free text, and browsable by faceting, tag, community, and collection exploration.

Data publication in MDF follows a workflow as shown in Figure 13.1. From the users data publication dashboard, which also displays information on the users prior and pending publications, the user chooses to initiate a new publication. The user then chooses the appropriate collection to publish the dataset into. Administrators can configure and customize the requirements for a collection with settings such as customized metadata fields, specified curation workflow (e.g. each submission must be reviewed by the collection administrator), and a specified data storage location. After selecting the appropriate collection for his publication, the user enters the predefined, collection-specific metadata (e.g. Datacite or domain-specific fields). Following this step, the dataset is assembled using Globus transfer to move selected files to a folder that is created on the collection-specified storage. The user assembles the dataset asynchronously using Globus transfer, and may return to complete the dataset submission when the transfer of the data is complete. Upon completion of dataset assembly, the user is presented with a summary page to confirm publication details (i.e. both data contents and metadata records) and once accepted, the dataset is optionally routed through the specified curation workflow.

After the dataset curation workflow is complete, the dataset is indexed and discoverable with external dataset access granted as determined by the collections pre-determined access control policy. Free text search and automatically generated facets on the MDF portal page help users find the datasets they are searching for. An example of a free text MDF search is shown in Figure 13.2. Matching datasets are returned as results and facets on author and subject are generated to help users navigate through the result set.

13.3 Future Outlook

A primary goal of MDF is to provide simple, reliable, and robust services tailored to the specific needs of the materials science community. Towards that end, it is critical to build relationships and interact with materials scientists in a variety of disciplines to understand their publication, discovery, and data sharing requirements, and to understand search requirements and other features of the associated use cases. We plan to enhance search and discovery capabilities by allowing users to specify which metadata attributes are indexed, which are shown as facets, and which are displayed in search results and summary pages. As a longer-term goal, we will seek to expand the flexibility of the metadata model

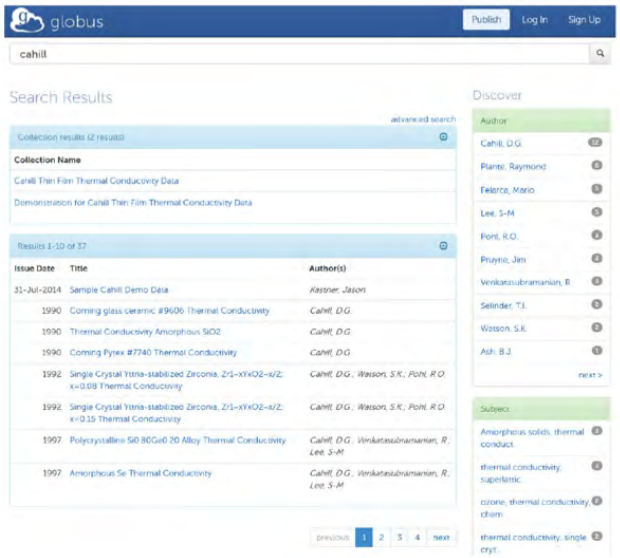


Figure 13.2: Searching across MDF collections by free text. Search results, comprised of published datasets, are shown on the left with additional facets on subject and author to allow quick navigation through the results

to support metadata objects, to allow typed metadata, and to support per-file specified metadata. We are also working to make many of the MDF features accessible via REST API to support programmatic access to published data, associated curation workflows, and to the exposed discovery features. These APIs will support a variety of new use functionality including automated ingest of metadata from file types that are critical to materials science to minimize the amount of metadata that scientists need to add manually.

13.4 NIST Collaborations

General Metadata Schema for Describing Materials Data Resources

*Ian **Foster** (UC/ANL), Robert Hanisch (NIST), Chandler Becker (NIST), Raymond Plante (NIST)*

In collaboration with Hanisch (NIST), Becker (NIST), and Plante (NIST), we are working to iteratively draft, adopt, and provide feedback on a general metadata schema for describing materials data resources. A general metadata schema would provide a standardized set of fields to ingest and index, and provide a starting point for building specialized custom metadata schemas.

Synergy with NIST Efforts

*Ian **Foster** (UC/ANL), Mary Brady (NIST), Alden Dima (NIST), Carelyn Campbell (NIST), Sharief Youssef (NIST)*

In collaboration with Brady (NIST), Dima (NIST), Campbell (NIST), and Youssef (NIST), we are in the early stages of investigating the potential to build a deeper connection between the MDF data publication service and the NIST Materials Data Curation System (MDCS) and we are working to deploy a Materials Resource Registry (MRR) instance to catalog and make discoverable relevant software, databases, and APIs.

13.5 Technology Transfer

Data Services

Materials Data Facility

I. Foster, S. Tuecke, B. Blaiszik, K. Chard, J. Pruyne, M. Ondrajcek

Access Link: https://materialsdatafacility.org

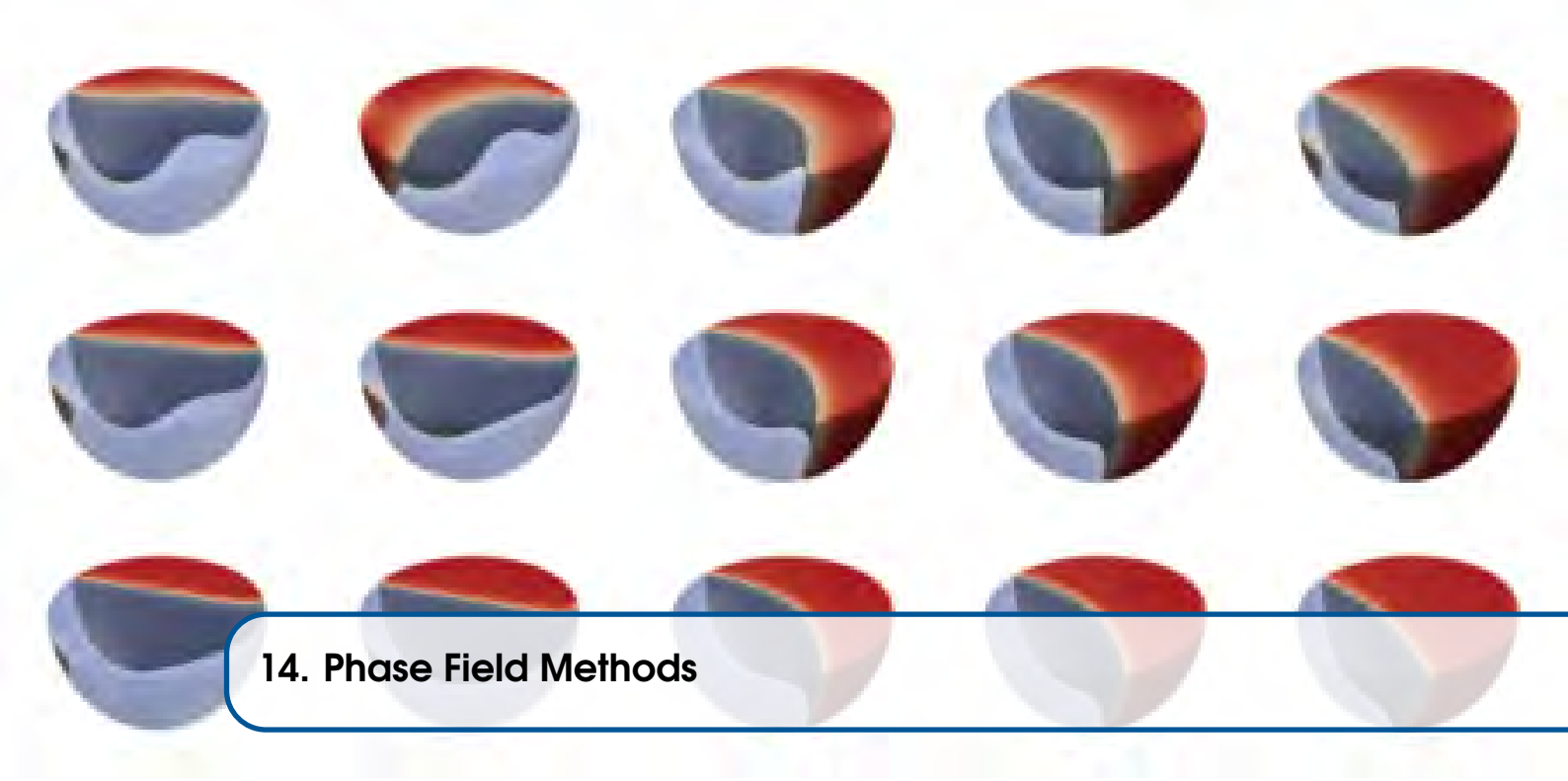
13.6 Publications and Presentations

2 Number of CHiMaD-supported publications in 2015 by Materials Data Facility Developers. Please see chapter 20 for details. [33, 34]

5 Number of presentations on CHiMaD supported research in 2015, please see section 21.9 for the complete list.

13.7 CHiMaD Team

Materials Data Facility Developers		
Name	**Position**	**Affiliation**
Ian Foster	Principal Investigator	UC/CI
Steven Tuecke	Deputy Director	UC/CI - ANL/MCS
Benjamin Blaiszik	Software Developer	UC/CI - ANL/MCS
Kyle Chard	Senior Researcher/Fellow	UC/CI - ANL/MCS
Jim Pruyne	Senior Software Developer	UC/CI
Michal Ondrejcek	Research Programmer	UIUC/NCSA



14. Phase Field Methods

Olle Heionen (NU), **Peter Voorhees (NU)**, **David Chopp (NU)**, Barry Smith (ANL), Dmitry Karpeev (ANL)

Significance

Mesoscale materials modeling, that spans length and time scales larger than atomic but smaller than microscopic, is central to modeling materials structural evolution. This is particularly the case for systems in which several degrees of freedom, such as elastic strain and diffusion, are coupled in inhomogeneous materials structures. Phase field methods are one set of mesoscale approaches to deal with such systems. CHiMaD is advancing phase fields methods with a goal of having quantitatively predictive modeling capabilities for structural evolution of three-dimensional systems. The efforts span both development of computational methods, algorithms, and models, as well as developing community standard problems for benchmarking, verification, and validation of phase field codes.

14.1 *Research Tools*

3D Multiphysics Phase Field Model **Heinonen** developed a 3D multiphysics phase-field model to study phase segregation in LiFePO4 nanoparticles, of interest due to their high (dis)charge rates in battery electrode applications. Spinodal decomposition into Li-rich and -poor phases is modified and can be suppressed by mesoscopic effects, which influences the kinetic and mechanical performance of this material as a battery electrode. Elastic and structural constants, diffusivity, and surface energy are highly anisotropic and concentration dependent, necessitating a 3D treatment.

The model includes spinodal decomposition, anisotropic, concentration-dependent elastic moduli, misfit strain, and facet dependent surface wetting within a Cahn-Hilliard framework. We simulated 3D spherical particles of radii from 3 nm to 40 nm and examined the equilibrium microstructure and voltage profiles as a they depend on size and overall lithiation. Our results show that the miscibility gap vanishes for particles of radius approximately 5 nm, and the solubility limits change with overall particle lithiation. Surface wetting stabilizes minority phases by aligning them with energetically beneficial facets.

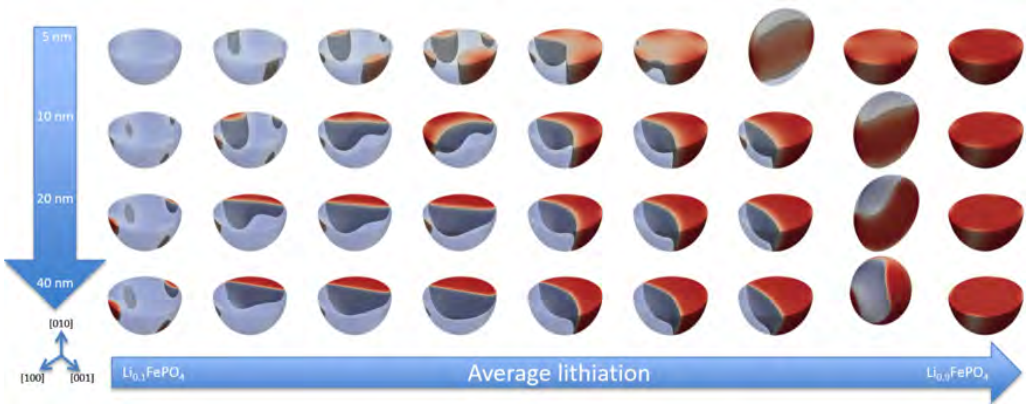


Figure 14.1: Summary of simulation results including surface wetting showing microstructural evolution as a function of particle radius and average concentration. Only results with the lowest free energy are shown. Surface wetting causes (de)lithiation of certain areas of the surface and competes with interfacial area minimization and anisotropic elasticity for dominance in determining the form and symmetry of the microstructure. Symmetries change for higher concentration x and are absent for the 40 nm $Li_{0.8}FePO_4$ particle.

Our results point to avenues to further improve the performance of Li_xFePO_4 nanoparticle electrodes by engineering surfaces with coating or geometry to affect the surface wetting.

Heinonen also developed a model for core-shell nanoparticles to study how the band gap is distributed in the nanoparticle, and how it can be affected by particle size and grain orientation, as well as by external pressure. In particular the band gap of Zn-ZnO core-shell nanoparticles are amenable to band gap modifications.

Community Standard Phase Field Codes The Phase Field Methods seed group researchers **Heinonen, Voorhees** are working on developing Phase Field Benchmark problems for community code development and benchmarking, in collaboration with Warren (NIST), Guyer (NIST), **Smith**, **Karpeev**. They have brought together an elite team of Phase Field experts and framework developers at the CHiMaD Phase Field Methods Workshops. Please see 19.4 for more information.

2D Locally Adaptive Time Stepping Method for Phase Field Simulations **Chopp** group developed the first 2D implementation of the Locally Adaptive Time Stepping Method (LATS), and applied it to solving the Cahn-Hilliard equation with periodic boundary conditions. Currently, the use of the LATS method for this equation is being explored as a means of enabling longer simulations for the phase field model by concentrating computational effort just on the subdomains where interfaces are present. Subdomains that are primarily only one phase will be updated orders of magnitude less often compared to subdomains where the interface is still present. Thus, as the phases coalesce, the method will get increasingly more efficient.

The LATS method was originally developed for one-dimensional domains, so the challenge is to ensure that the more complex boundary conditions between subdomains in a higher dimensional setting would still work. For testing purposes, a stripe domain decomposition was used in order to make communications simpler. **Chopp** group demonstrated both that (1) the method preserves the stability properties of the underlying backward difference formula time stepping method, (2) the version with domain decomposition gave the same results as the corresponding serial implementation, and (3) the method scales appropriately

on a parallel architecture. A version with rectangular domain decomposition is expected to be complete by the end of CHiMaD Year Two, after which benchmark testing for optimal time steps will begin.

14.2 Collaborations

14.2.1 NIST Collaborations

Phase Field Benchmark Problems
*Olle **Heinonen** (ANL), Peter **Voorhees** (NU), James Warren (NIST), Jonathan Guyer (NIST)*
This collaboration aims to develop phase field benchmark problems for the global phase field community.

14.2.2 External Collaborations

Scalable Computational Models and Codes
*Olle **Heinonen** (ANL), Serge Nakhmanson (University of Connecticut)*
Through this collaboration scalable computational models and codes for coupled ferroelectric-elastic systems are being developed.

Scalable Computational Models and Codes
*Olle **Heinonen** (ANL), Michael Welland (Chalk River National Laboratory, Canada)*
This collaboration concentrated on developing phase field models for coupled diffusion-elasticity problems.

14.3 Publications and Presentations

2 Number of CHiMaD-supported publications in 2015 by Additive Manufacturing seed group. Please see chapter 20 for details. [35, 36]

3 Number of presentations on CHiMaD supported research in 2015, please see section 21.12 for the complete list.

2 Phase Field Methods seed group has organized the CHiMaD Phase Field Methods Workshop I-II and the CHiMaD Phase Field Hackathon. Please see 19.4 for more information.

14.4 CHiMaD Team

Phase Field Methods Group Researchers			
Name	**Position**	**Affiliation**	**Project (PI)**
Olle Heinonen	Principal Investigator	ANL /NAISE	
Peter Voorhees	Principal Investigator	NU/MSE	
David Chopp	Principal Investigator	NU/ESAM	
Dmitry Karpeev	Principal Investigator	ANL /NAISE	
Barry Smith	Principal Investigator	ANL /NAISE	
Andrea Jokisaari	Postdoctoral Researcher	NU/NAISE	Mesoscale modeling of microstructural evolution *(Heinonen)*
Narut Sereewattanawoot	Graduate Student	NU/ESAM	LATS method for phase field simulations *(Chopp)*

V

Other

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19 CHiMaD Outreach 141

15. Honors & Awards

Hadallia Bergeron (NU)
Hierarchical Materials Cluster Program Graduate Fellowship
The Graduate School
Northwestern University

Wei Chen (NU)
Design Automation Award *(the highest achievement award in design automation)*
Design Engineering Division
American Society of Mechanical Engineers (ASME)

Mark Hersam (NU)
World Technology Network Fellow
The World Technology Network

Sinan Keten (NU)
ONR Young Investigator Program Award
Office of Naval Research

David Seidman (NU)
ASM International Edward DeMille Campbell Memorial Lectureship
Material Science and Technology meeting
Columbus, OH, USA(10/07/15)

Steven Sibener (UC)
Dedicated Festschrift Issue in his honor
36 manuscripts from groups located worldwide
Journal of Physical Chemistry C
J. Phys. Chem. C., July 2 Issue, Vol. 119, No. 26 (2015)

Juan de Pablo (UC)
Elected into National Academy of Engineering
For design of macromolecular products and processes via scientific computation

Juan de Pablo (UC)
Elected into Mexican Academy of Sciences
Mexican Academy of Sciences

Juan de Pablo (UC)
Delivered Alumni Lectures
University of Massachusetts

Juan de Pablo (UC)
Delivered Peck Lectures
Illinois Institute of Technology

Juan de Pablo (UC)
Keynote Address
8th PPEPPD (Property and Phase Equilibria for Predictive Process Design) International Conference
Porto, Portugal

Juan de Pablo (UC)
Founding Editor
Molecular Systems Design and Engineering

Alexander Umatsev (FSU)
2015-2016 Fulbright U.S. Scholar Award
J. William Fulbright Foreign Scholarship Board

Peter Voorhees (NU)
Van Vlack Lectures
Department of Materials Science and Engineering
University of Michigan

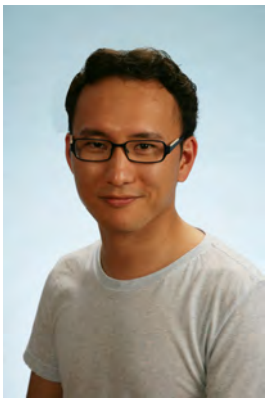
Peter Voorhees (NU)
Hillert-Cahn Lectures
International Conference on solid-Solid Phase Transformations
Whistler, Canada

Logan Ward (NU)
Weertman Fellowship
Department of Materials Science and Engineering
Northwestern University

Zonghui Wei (NU)
Ryan Fellowship
The Graduate School
Northwestern University

Huanxin Wu (NU)
Fellowship
Center for Computation and Theory of Soft Matter
Northwestern University

16. NIST-CHiMaD Postdoctoral Research Fellows



Marat Andreev (UC/NIST)

Soft Matter Design Based on Charge Complexation

Supervisors: Juan De Pablo (UC), Jack Douglas (NIST)

Bio Dr. Andreev was born in Siberia, Russia. He received his B.Sc and M.Sc degrees from Novosibirsk State University. In 2009 he joined Professor Jay Schieber's research group at Illinois Institute of Technology and was awarded his Ph.D. in December 2014. He then joined the ***De Pablo*** *group at University of Chicago as postdoctoral researcher; in 2015 he was awarded a NIST-CHiMaD postdoctoral research fellowship.*

Research Polyelectrolyte coacervation refers to the formation of distinct liquid phases that arise when polycations and polyanions are mixed under appropriate polymer and salt concentrations. Molecular-level studies of complex polyelectrolyte coacervation have been limited. Under supervision of **de Pablo**, a computationally efficient soft-core model of the polymers and the corresponding counterions is proposed. The model is used to simulate coacervation as a function of polymer length and overall salt concentration. The model is shown to reproduce a number of phenomena observed in experiments, including the destabilization of the coacervate by increasing ionic strength of by decreasing molecular weight. The results of the soft-core model are also shown to compare favorably with those of a more traditional representation that relies on hardcore potentials. Self-assembly of coacervate in the model is studied under supervision of Douglas (NIST) during my stay at NIST. A manuscript based on this work is in preparation.

The soft-core models, such in Figure 16.1, have limitations for application to dense polymeric systems. Particularly, it is commonly accepted that polymer chains over a certain molecular weight form so-called entanglements-topological constraints that chains exert on each other. These entanglements are further believed to govern the macroscopic behavior of polymeric systems. It is possible to capture many important physical details with atomistic simulations, but modern computations are unable to reach the long relaxation times observed for entangled system, which can reach minutes or hours. However, it is possible to include entanglement effect in a soft-core model via slip-springs. In **de**

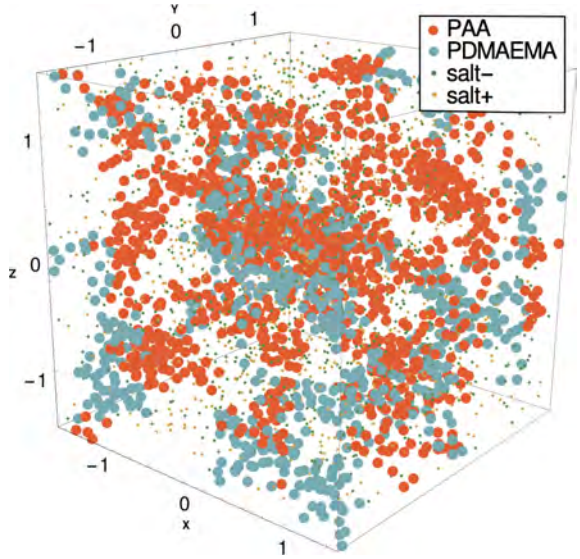
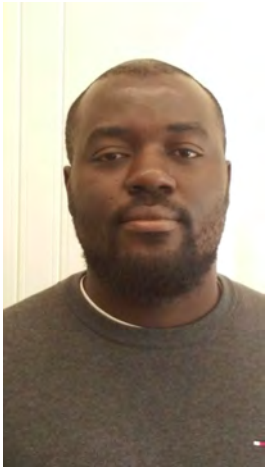


Figure 16.1: Self-assembled coacervate complex in the center of the simulation box. Here soft-core model, same concentrations of polymers and salt is used.

Pablo group the *Theoretically Informed Entanglement Polymer Simulations* Slip-Spring model was proposed. Since I joined the group several important modifications were made to the model, which allowed to avoid few issues of the previous implementation. The modified model is applied to homopolymer linear and non-linear rheology and to simulations of entangled diblock copolymers with great success. The ultimate goal of my work on the model is enabling straight-forward mapping of parameters from detailed (atomistic) simulations, while newly developed GPU algorithm provides a way to perform simulation long enough to capture entanglement relaxation. The dynamic observables soft-core slip-spring simulations are compared to the results of detailed simulations. The detailed simulation data is provided by Douglas (NIST). The paper based on this work is in preparation.



Nana Ofori-Opoku (NU/NIST)

Phase-Field Methods

Supervisors: Peter Voorhees (NU), James Warren (NIST)

Bio Dr. Ofori-Opoku holds a Ph.D. from the Materials Science and Engineering Department, McMaster University. While completing his Ph.D., he held multiple appointments as visiting researcher at TKK Aalto University and VTT Technical Research Centre in Finland. Before joining CHiMaD as a NIST-CHiMaD Postdoctoral Research Fellow, he was a postdoctoral fellowship at McGill University working on recrystallization kinetics and microstructure development for nanoscale devices using continuum and atomistic models. His research interests combine computational materials science and condensed matter physics, with emphasis on multi-scale modeling of non-equilibrium materials phenomena and microstructure evolution.

Research Developing a phase field model of faceted eutectic growth to produce a predictive model for describing microstructure and spacing selection as a function of the processing conditions. This is in collaboration with **Voorhees** (NU) and Warren (NIST). We have opted to use the more atomistic phase field crystal methodology, as describing faceted structures require atomic scale resolution. In doing so, we are now working on validating the phase field crystal methodology, for single component systems, applied to faceted solidification structures. The model is currently being tested and validated for its capabilities in quantitatively and accurately describing faceted microstructures and their behavior. Thus far, the initial investigation is garnering insights into such behavior, e.g. surface energetics, growth modes, and out-of-equilibrium kinetics. These insights are then going to be used, shortly, in developing an alloy phase field crystal model for a faceted eutectic study.

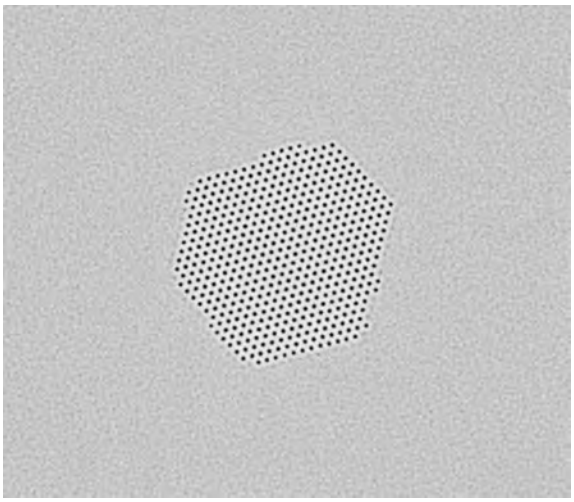
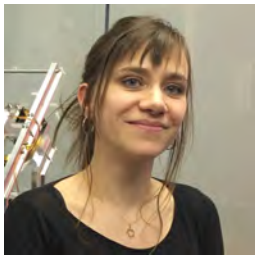


Figure 16.2: Simulation of out of equilibrium solidification of a faceted crystal in the presence of thermal fluctuations. The atomic probability density of the crystal lattice is shown. Clearly shown is the ledge nucleation and growth mechanism, a hallmark of faceted systems.



Fanny Rodolakis Simoes (ANL/NIST)

Directed Self-Assembly of Block Copolymers Films for Lithographic Applications

Supervisors: Paul Nealey (UC), Joseph Kline (NIST)

Bio Dr. Rodolakis Simoes received her Ph.D. in physics from University Paris-Sud in 2009 for investigating the metal insulator transitions in vanadium oxides combining different synchrotron based X-ray techniques: photoemission, X-ray absorption and inelastic scattering. During her post-doctoral experience at the University of Illinois in Chicago and the Materials Science Division at ANL, she continued an interest in strongly correlated systems using angle resolve photoemission spectroscopy (ARPES) to investigate the Fermi surface collapse and hybridization effects in Ce-based heavy fermion compounds. In 2014 she was awarded a NIST-CHiMaD postdoctoral research fellowship at the new Intermediate Energy (250-2500 eV) X-ray beamline where she is now an assistant physicist. This beamline will utilize resonant soft x-ray scattering (RSoXS) and ARPES to probe order and disorder in emergent materials. Those materials include structural ordered systems such as directed self-assembly of block copolymers and spin ices.

Research Dr. Rodolakis Simoes' main project was the commissioning of the new Intermediate Energy X-ray (IEX) beamline at Sector 29 of the Advanced Photon Source (APS) at ANL, and in particular the development of a resonant soft x-ray scattering capability for directed self-assemblies block copolymer systems. She performed first scattering experiment at IEX, successfully testing the feasibility of carrying out resonant soft X-ray scattering (RSoXs) on directed self-assembly (DSA) block copolymer in collaboration with Kline (NIST): Figure 16.3 shows the very first diffraction pattern measured at the IEX scattering end-station on a patterned polymer sample infiltrated with aluminum oxide using the delay-line microchannel plate detector. The fact that both the specular and the first order diffraction peak can be seen proves that the detector has the required dynamic range for the study of buried structure of DSA. She also collaborated with Kline (NIST) to implement *on the fly* RSoXS data analysis tools at the IEX beamline. She rebuilt and optimized the scattering in-vacuum Kappa diffractometer at the IEX beamline, minimizing the sphere of confusion, improving robustness and adding limit switches to avoid crashes. Designed and commissioned a new sample stage allowing measurements in transmission. She continued the on-going commissioning of the beamline to fully characterized the x-ray beam at the sample. Developed user interfaces tools for the beamline and the endstation. As a new beamline scientist at IEX, she plans to continue collaborating with **Nealey** (UC) group to make IEX a local destination for RSoXS on DSA.

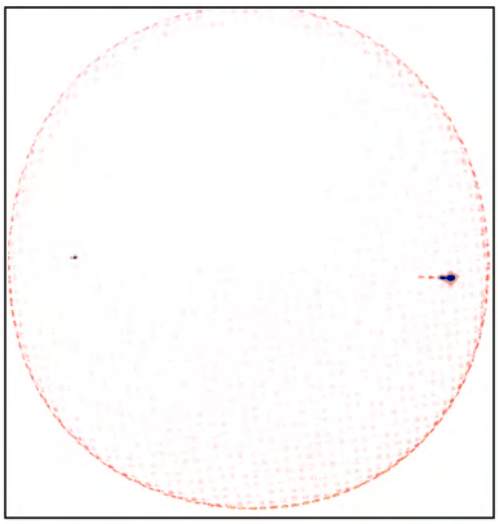


Figure 16.3: Specular (right) and 1st order (left) diffraction peaks taken on a patterned polymer sample infiltrated with aluminum oxide at the IEX beamline

Peisheng Wang (NU/NIST)

Precipitation Strengthened Alloys

Supervisors: Gregory Olson (NU), Ursula Kattner (NIST), Carelyn Campbell (NIST), Eric Lass (NIST)

Bio Dr. Wang's main research interest lies in thermodynamic calculations (CALPHAD). He received his Ph.D. in 2012 from Central South University, China for experimental determination of Mg phase diagram and thermodynamic calculations. He was then a postdoctoral researcher at TU Clausthal, Germany between 2012-2014. During his postdoctoral work he was interested in Heterogeneous Nucleation and Microstructure Formation of Al-Cu-Ni alloys and a new function to describe the Gibbs energy of liquid phase. In 2015 he was awareded a NIST-CHiMaD Postdoctoral Research Fellowship to futher CALPHAD methods under Precipitation-Strengthened Alloys use-case group.

Research Dr. Wang is working to establish a multicomponent thermodynamic database for the Co-based superalloy; his prime focus is the Co-Al-W-Ta-Ti-Ta system. Applications of traditional Co-based alloys suffer from lower high-temperature strength compared to Ni-base alloys. The L12 γ' phase Co3(Al,W), exhibit a considerable improvement in high-temperature strength, indicating a promising future for the Co superalloys. However, consequent experiments by Lass (NIST) show that the ternary γ' phase Co3(Al,W) is a thermodynamically unstable phase, unless additional elements are added for stabilizing the γ' phase. Therefore, a multicomponent Co database with rigorous thermodynamics description of phase stability of the γ' phase can facilitate Co-Al-W based superalloy design. Dr. Wang's main accomplishments in CHiMaD Year Two are: (1) The Co-Al, Co-W, Co-Ta, Al-W and Al-Ni systems are critically reviewed and reassessed by cooperating density functional theory (DFT) calculations. The critical γ' phase was described as metastable phase in Co-Al, Co-W and Al-W systems; (2) A thermodynamic database for Co-Al-W-Ni-Ti-Ta system including all the binaries is now deliverable. More complex and accurate sublattice models were used in the present database compared to the other available multi-component database. For example, four sublattice order-disorder transition models have been used to describe both B2 and L12 structures. One of the representative accomplishments is the optimization for the Co-W system, as shown in Figures 16.4.

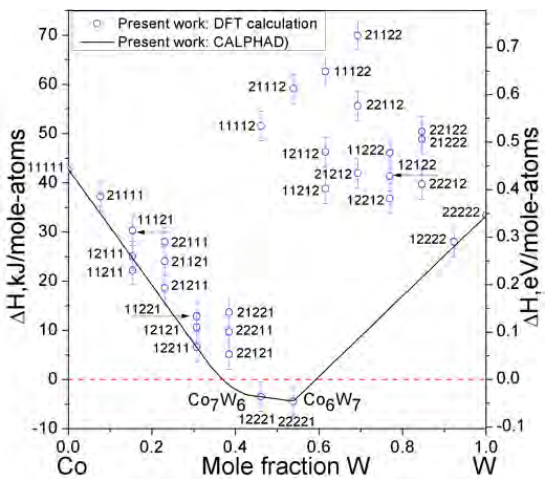


Figure 16.4: Calculated CALPHAD enthalpy of formation of the μ phase compared to first-principles (FLAPW) results. The reference state is Hcp Co (non-magnetic) and Bcc W. The open blue circles are the calculated enthalpy of formation for all the end-members of μ phase. The composition of each end-member is presented by a five-digit number like 22122, where 1 corresponds to Co and 2 to W, and the order of digits reflect the occupancy of the corresponding sublattices in the following order: Co1(3a)-W1(6c1)-W2(6c2)-W3(6c3)-Co2(18h). For example, 12221 corresponds to the nominal μ-phase Co7W, 22221 - the "new" μ-phase Co6W7. The error bar for the FLAPW results is $\pm$3kJ/mole-atoms (or 0.03 eV/mole-atoms).

17. CHiMaD Principal Investigators and Staff

17.1 CHiMaD Principal Investigators

Peter Voorhees
CHiMaD Co-Director
Frank C. Engelhart Professor of Materials Science and Engineering
Department of Materials Science and Engineering
Northwestern University

Gregory Olson
CHiMaD Co-Director
Walter P. Murphy Professor of Materials Science and Engineering
Department of Materials Science and Engineering
Northwestern University

Juan De Pablo
CHiMaD Co-Director
Liew Family Professor in Molecular Engineering
Institute for Molecular Engineering
University of Chicago

Ankit Agrawal
Research Associate Professor
Department of Electrical Engineering and Computer Science
Northwestern University

Micheal Bedyzk
Department Chair and Professor of Materials Science and Engineering
Department of Materials Science and Engineering
Northwestern University

Larry Berardinis
Technology Projects Manager, Computational Materials Data (CMD) Network
ASM International

Ida Berglund
Materials Design Engineer

QuesTek Innovations LLC

Catherine Brinson
Jerome B. Cohen Professor of Mechanical Engineering
Associate Dean for Academic and Professional Initiatives
Department of Mechanical Engineering
Northwestern University

Jian Cao
Associate Vice President of Research
Director of Northwestern Initiative for Manufacturing Science and Innovation (NIMSI)
Professor of Mechnical Engineering
Department of Mechanical Engineering
Northwestern University

Wei Chen
Wilson-Cook Professor in Engineering Design
Professor of Mechanical Engineering
Department of Mechanical Engineering
Northwestern University

Alok Choudhary
Henry Isabelle Dever Professor of Electrical Engineering and Computer Science
Department of Electrical Engineering and Computer Science
Northwestern University

Yip-Wah Chung
Professor of Materials Science and Engineering
Department of Materials Science and Engineering
Northwestern University

Ian Foster
Director, Computation Institute
Professor, Department of Computer Science
Senior Scientist, Mathematics and Computer Science Division
University of Chicago
Argonne National Laboratory

Giulia Galli
Liew Family Professor in Molecular Engineering
Institute for Molecular Engineering
University of Chicago

Olle Heinonen
Strategic Initiative Lead in Computational Chemistry and Materials
Materials Scientist
Fellow, Northwestern-Argonne Institute of Science and Technology
Materials Science and Engineering Division
Argonne National Laboratory

Scott Henry
Director, Content & Knowledge-Based Solutions
ASM International

Mark Hersam
Walter P. Murphy Professor of Materials Science and Engineering
Director, Materials Research Science and Engineering Center (MRSEC)
Department of Materials Science and Engineering
Northwestern University

Heinrich M. Jaeger
William J. Friedman and Alicia Townsend Professor of Physics
James Franck Institute and Department of Physics
University of Chicago

Dmitry Karpeev
Assitant Computational Mathematician
Fellow, Computation Institute
Mathematics and Computer Science Division
Argonne National Laboratory

Sinan Keten
Assistant Professor of Mechanical Engineering
Assistant Professor of Civil and Environmental Engineering
Department of Mechanical Engineering
Department of Civil and Environmental Engineering
Northwestern University

Lincoln Lauhon
Professor of Materials Science and Engineering
Department of Materials Science and Engineering
Northwestern University

Wing-Kam Liu
Walter P. Murphy Professor of Mechanical Engineering & Civil and Environmental Engineering
Department of Mechanical Engineering
Department of Civil and Environmental Engineering
Northwestern University

Erik Luijten
Professor of Materials Science and Engineering
Department of Materials Science and Engineering
Engineering Sciences and Applied Mathematics
Northwestern University

Tobin J. Marks
Charles E. and Emma H. Morrison Professor of Chemistry
Professor of Materials Science and Engineering
Vladimir N Ipatieff Professor of Catalytic Chemistry
Department of Chemistry
Northwestern University

Sid Nagel
Stein-Freiler Distinguished Service Professor
James Franck Institute and Department of Physics
University of Chicago

Paul Nealey
Brady W. Dougan Professor in Molecular Engineering
Institute for Molecular Engineering
University of Chicago

James Saal
Sr. Materials Design Engineer
QuesTek Innovations LLC

Jason Sebastian
Director of Technology
QuesTek Innovations LLC

Steven Sibener
Carl William Eisendrath Distinguished Service Professor
Department of Chemistry and The James Frank Institute
University of Chicago

Barry Smith
Senior Computational Mathematician
Senior Fellow, Northwestern-Argonne Institute of Science and Technology
Mathematics and Computer Science Division
Argonne National Laboratory

David Snyder
Sr. Materials Development Engineer
QuesTek Innovations LLC

Matthew Tirrell
Dean and Founding Pritzker Director
Institute for Molecular Engineering
University of Chicago

Monica Olvera de la Cruz
Lawyer Taylor Professor of Materials Science and Engineering
Department of Materials Science and Engineering
Northwestern University

Alexander Umantsev
Professor of Physics
Department of Chemistry and Physics
Fayetteville State University

Christopher Wolverton
Professor of Materials Science and Engineering
Department of Materials Science and Engineering
Northwestern University

Luping Yu
Professor of Chemistry
Department of Chemistry
University of Chicago

17.2 CHiMaD Technical Staff

Emine Begum Gulsoy
CHiMaD Associate Director
Fellow, Northwestern-Argonne Institute of Science and Engineering
Research Associate
Department of Materials Science and Engineering
Northwestern University

Laura Bartolo
CHiMaD Data & Database Efforts Coordinator
Northwestern-Argonne Institute of Science and Engineering
Northwestern University

Ricardo Komai
CHiMaD Materials Design Expert
Postdoctoral Researcher
Department of Materials Science and Engineering
Northwestern University

17.3 CHiMaD Administrative Staff

Goldie Gorski
Director of Operations and Outreach
Northwestern-Argonne Institute of Science and Engineering
Northwestern University

Deneen Marie Bryce
Business Administrator
Northwestern-Argonne Institute of Science and Engineering
Northwestern University

Janet Boland
Executive Assistant
Institute for Molecular Engineering
University of Chicago

Kathleen Bennett
Program Assistant
Northwestern-Argonne Institute of Science and Engineering
Northwestern University

18. CHiMaD NIST Collaborators

James Warren
Techincal Program Director, Materials Genomics
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Debra Audus
Chemical Engineer, Polymers and Complex Fluids Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Chandler Becker
Materials Research Engineer, Thermodynamics and Kinetics Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Mary Brady
Group Leader, Information Systems Group
Software and Systems Division
Information Technology Laboratory
NIST, Gaithersburg, MD

Benjamin Burton
Research Scientist, Thermodynamics and Kinetics Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Carelyn Campbell
Group Leader, Thermodynamics and Kinetics Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Chelsea Davis

NRC Postdoctoral Fellow, Polymers and Complex Fluids Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Albert Davydov
Leader, Functional Nanostructured Materials Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Alden Dima
Research Scientist
Software and Systems Division
Information Technology Laboratory
NIST, Gaithersburg, MD

Jack Douglas
NIST Fellow
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Aaron Foster
Materials Research Engineer, Polymeric Materials Group
Materials and Structural Systems Division
Engineering Laboratory
NIST, Gaithersburg, MD

Douglas Fox
Guest Researcher, Flammability Reduction Group
Fire Research Division
Engineering Laboratory
NIST, Gaithersburg, MD

Jeffrey Gilman
Polymer Chemist, Polymers and Complex Fluids Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Jonathan Guyer
Group Leader, Mechanical Performance Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Robert Hanish
Director
Office of Data and Informatics
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Adam Hannon
NRC Postdoctoral Fellow, Functional Polymers Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Ursula Kattner
Physical Scientist, Thermodynamics and Kinetics Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Ketan Khare
Postdoctoral Researcher, Polymers and Complex Fluids Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Joseph Kline
Project Leader, Functional Polymers Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Kenneth Kroenlein
Director, Thermodynamic Research Center
Applied Chemicals and Materials Division
NIST, Boulder, CO

Sergiy Krylyuk
Guest Researcher, Functional Nanostructured Materials Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Eric Lass
Materials Research Engineer, Thermodynamics and Kinetics Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Lyle Levine
Project Leader, Additive Manufacturing of Metals
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Alexander Liddle
Deputy Director (Acting) and Group Leader
Nanofabrication Research Group
Center for Nanoscale Science and Technology
NIST, Gaithersburg, MD

Li Ma
Guest Scientist, Mechanical Performance Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Kil-Won Moon
Postdoctoral Researcher, Thermodynamics and Kinetics Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Sarala Padi
Research Scientist
Software and Systems Division
Information Technology Laboratory
NIST, Gaithersburg, MD

Adele Peskin
Research Scientist
Software and Systems Division
Information Technology Laboratory
NIST, Gaithersburg, MD

Frederick Phelan
Chemical Engineer, Polymers and Complex Fluids Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Raymond Plante
Research Scientist
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Vivek Prabhu
Chemical Engineer, Polymers and Complex Fluids Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Lee Richter
Physicist, Functional Polymers Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Deepak Sharma
Guest Researcher, Functional Nanostructured Materials Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Arunima Singh
Guest Researcher, Thermodynamics and Kinetics Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Mark Stoudt
Materials Research Engineer
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Francesca Tavazza
Research Scientist, Thermodynamics and Kinetics Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Maureen Williams
Materials Scientist, Thermodynamics and Kinetics Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Jonathan Winterstein
Research Scientist, Nanofabrication Research Group
Center for Nanoscale Science and Technology
NIST, Gaithersburg, MD

Jeremiah Woodcock
Research Chemist, Polymers and Complex Fluids Group
Materials Science and Engineering Division
Materials Measurement Laboratory
NIST, Gaithersburg, MD

Sharief Youssef
Research Scientist
Software and Systems Division
Information Technology Laboratory
NIST, Gaithersburg, MD

19. CHiMaD Outreach

When Materials Genome Initiative was put forth by the White House in 2011, the three pillars of the initiative were described as: (1) Developing a open-access and open-source materials innovation infrastructure, (2) Achieving national goals with advanced materials using this infrastructure, (3) Equipping the next generation materials workforce in government, academia and industry. [https://www.whitehouse.gov/sites/default/files/microsites/ostp/materials_genome_initiative-final.pdf]. CHiMaD workshops are designed and organized with these three major goals of the MGI in mind with an emphasis on training the current and next generation of government, industrial and academic researchers with the right tools to make MGI a sustainable success.

Towards this goal, in 2015, CHiMaD organized an MGI Seminar series, welcoming an international group of researchers to present about their MGI-related efforts as well as other international MGI initiatives they are a part of. This series of presentations were broadcast to all CHiMaD partner institutions (Section 19.1). In accordance with the goal of equipping the next generation of researcher and in collaboration with ASM International Educational Committee, CHiMaD initiated the dissemination of some of the most significant current materials design software to engineering universities in the U.S. where the universities are expected to build these tools into their undergraduate curriculum. In its first round, proposals by six universities were awarded (Section 19.2). CHiMaD also took the lead in the organization of various high-impact workshops aiming at community building and bridging for collaborations and open-access exchange of knowledge on their topics of interest (Section 19.4). This chapter, therefore, provides an overview of the CHiMaD Outreach activities in 2015.

19.1 MGI Seminar Series

All CHiMaD seminar abstracts, presenter biographies and event fliers are available on the CHiMaD Event Archives at http://chimad.northwestern.edu/news-events/Event_Archives.html

03/24/15 - *CHiMaD HQ & Broadcast*
TMS Initiatives Related to ICME/MGI, Manufacturing, and Energy
George Spanos
Technical Director, TMS

04/30/15 - *CHiMaD HQ & Broadcast*
Low-Dimensional Semiconductors for Electronics, Sensors, and Energy
Albert Davydov
Group Leader, Functional Materials Group
National Institute of Standards and Industry

04/30/15 - *CHiMaD HQ & Broadcast*
TCombining X-Ray Scattering and Materials Modeling for Directed Self-Assembly Morphology Measurements
Joseph Kline
Project Leader, Functional Polymers Group
National Institute of Standards and Industry

06/23/15 - *CHiMaD HQ & Broadcast*
Elucidating the Role of Boron in Extending Persistence Eu^{2+} and Dy^{3+} Co-doped $Sr_4Al_{14}O_{25}$ by Cathodoluminescence, STEM-EDX and Electron Diffraction
Cleva Ow-Yang
Professor, Department of Materials Science and Engineering
Sabanci University, TURKEY

06/25/15 - *CHiMaD HQ & Broadcast*
Bio-inspired Self-healing Ceramics for Turbine Blade Applications
Toshio Osada
Researcher, Structural Materials Unit
National Institute for Materials Science (NIMS), JAPAN

07/27/15 - *Northwestern University*
From Atoms to Alloy Engineering Behaviour
David Dye
Professor, Department of Materials Science and Engineering
Imperial College London, ENGLAND

07/31/15 - *CHiMaD HQ & Broadcast*
Multi-scale Simulation of Steel and Aluminum Alloy Sheets using Phase Field and Crystal Plasticity Finite Element Methods: From Microstructure to Sheet Metal Forming
Akinori Yamanaka
Assistant Professor, Department of Mechanical Systems Engineering
Tokyo University of Agriculture and Technology, JAPAN

08/19/15 - *CHiMaD HQ & Broadcast*
Multi-scale Finite Element Modeling in Structural Metals
Ikumu Watanabe
Senior Researcher
National Institute for Materials Science (NIMS), JAPAN

09/17/15 - *CHiMaD HQ & Broadcast*
Studying the Micromechanics of Marthensitic Phase Transformations Using High Energy

Diffraction Microscopy
Aaron Stebner
Assistant Professor, Department of Materials Science and Engineering
Colorado School of Mines

09/21/15 - *CHiMaD HQ & Broadcast*
Electrochemistry on Nano- and Atomic Levels: Scanning Probe Microscopy Meets Deep Data
Sergei V. Kalinin
Director, Institute for Functional Imaging of Materials
Distinguished Research Staff Member, Center for Nanophase Materials Sciences
Oak Ridge National Laboratory

09/22/15 - *Argonne National Laboratory*
Big, Deep, and Smart Data in Energy Materials Research: Atomic View on Materials Functionalities
Sergei V. Kalinin
Director, Institute for Functional Imaging of Materials
Distinguished Research Staff Member, Center for Nanophase Materials Sciences
Oak Ridge National Laboratory

10/08/15 - *Fayetteville State University*
Atomistic Scale Modeling of Faceted Solidification and Microstructure Evolution
Nana Ofori-Opoku
NIST-CHiMaD Postdoctoral Research Fellow
Center for Hierarchical Materials Design
National Institute of Standards and Industry

11/11/15 - *CHiMaD HQ & Broadcast*
Vacuum Induction Melting and Vacuum Arc Remelting of Co-Al-W-X Gamma-Prime Superalloys
Erin T. McDevitt
Manager, Research and Development
ATI Specialty Materials

12/09/15 - *CHiMaD HQ & Broadcast*
NIMS Materials Database: Current Status and Future Prospects
Yibin Xu
Leader, Materials Database Group
National Institute for Materials Science (NIMS), JAPAN

12/14/15 - *CHiMaD HQ & Broadcast*
Towards Predictive *ab initio* Simulation of Surfaces and Interfaces
Ikutaro Hamada
MANA Researcher, International Center for Materials Nanoarchitectronics
National Institute for Materials Science (NIMS), JAPAN

19.2 ASM Materials Genome Toolkit

ASM International and its affiliate members administered a competition among undergraduate universities in the U.S., awarding six schools with state-of-the-art materials design software and related materials property databases. The competition was announced in early 2015 and broadly publicized via direct email, on the ASM and CMD Network websites, through several ASM newsletters, and in a press release issued to various news outlets and materials-oriented professional societies. Schools competed on the basis of a proposal stating how they planned to integrate the Materials Genome Toolkit software into their undergraduate curriculum and in the context of the annual ASM Undergraduate Design Competition. A review committee convened by the ASM Action in Education Committee, the subcommittee on Computational Materials Engineering, evaluated the entries, ranking them according to several factors, including the degree to which the proposed plan balanced theory and application in the use of the software.

ASM MGI Toolkit Awardees

California State Polytechnic University in Pomona
Lead PI: Vilupanur Ravi
Chemical and Materials Engineering
*1st Place, 2015 ASM Undergraduate Design Competition

Carnegie Mellon University
Lead PI: Bryan Webler
Department of Materials Science and Engineering
*2nd Place, 2015 ASM Undergraduate Design Competition

Michigan Technological Institute (*Pilot Program*)
Lead PI: Paul Sanders
Department of Materials Science and Engineering
*3rd Place, 2015 ASM Undergraduate Design Competition

Alfred University
Lead PI: S. K. Sundaram
Department of Materials Science and Engineering

University of Maryland
Lead PI: Yifei Mo
Department of Materials Science and Engineering

Virginia Polytechnic Institute and State University
Lead PI: Alan Druschitz
Department of Materials Science and Engineering

Colorado School of Mines (*Awarded through LIFT*)
Lead PI: Kip Findley
Department of Metallurgical and Materials Engineering

In the first round of the competition, six engineering schools were selected to receive the Toolkit, including Alfred University, California State Polytechnic University in Pomona, Carnegie Mellon University, Michigan Technological Institute, the University of Maryland, and Virginia Polytechnic Institute and State University. Each school now has a three-year, multi-user license, giving hundreds of students and faculty across the U.S. access to the latest Thermo-Calc thermodynamics code, DICTRA multicomponent diffusion code, TC-PRISMA precipitation simulator, and several thermodynamic and mobility databases. An equivalent software package has also been awarded to the Colorado School of Mines, one of the top seven finishers in the toolkit competition, under the auspices of the Lightweight Innovations for Tomorrow

(LIFT) consortium.

The CHiMaD-sponsored ASM Materials Genome Toolkit program is made possible by a NIST grant, the ASM Materials Education Foundation, and Thermo-Calc Software, which generously offered an 85% discount on what will ultimately be twelve sets of tools worth more than $1.6 million. The software distribution program addresses several CHiMaD objectives by helping the next generation of scientists and engineers become proficient with materials-by-design tools and techniques and by contributing to efforts that are advancing the collective knowledge on material systems and methodologies.

ASM is conducting a second Materials Genome Toolkit competition in the coming year that will award four more engineering schools with state-of-the-art materials design software. The application deadline for the proposals is April 30, 2016. As in the first round of the competition, ASM is promoting the contest to faculty and students through email, newsletters, web posts, community forums, AM&P magazine, and a broadcast press release. ASM will also publicly recognize the first ten MGI toolkit winners during an ASM function at Materials Science and Technology 2016 in Salt Lake City, Utah, and will work to develop metrics to capture and convey how the toolkit program is benefitting each school.

ASM Principal Investigators gave 9 presentations regarding the CHiMaD-ASM outreach activities in 2015 (see section 21.13).

19.3 Workshops and Meetings

The agendas for CHiMaD-organized and supported workshops are available on the CHiMaD Event Archives at http://chimad.northwestern.edu/news-events/Event_Archives.html

Phase Field Methods Workshop I
January 9, 2015 | Northwestern University
Phase Field Methods Hackathon
October 14, 2015 | CHiMaD Headquarters
Phase Field Methods Workshop II
October 15-16, 2015 | CHiMaD Headquarters
Organizers: Olle **Heinonen** (ANL), Peter **Voorhees** (NU)

Attendees of the CHiMaD Phase Field Methods Workshop II & Hackathon

Scope On January 9th, 2015, CHiMaD hosted a small workshop focused on starting a discussion regarding the development of a community standard phase field code, and to address how to include the varying needs of the community within these codes. This invitation-only workshop consisted of 18 world-leading experts and framework developers on phase field methods. A seed group lead by Olle **Heinonen** (ANL) and consisting of Peter **Voorhees** (NU), James Warren (NIST) and Jonathan Guyer (NIST) were nominated to determine a set of community benchmark problems over which the results of different phase field codes and frameworks from around the world could be directly compared.

A draft of these benchmark problems were created between January and October. On October 14, 2015 CHiMaD organized the CHiMaD Phase Field Methods Hackathon where teams of two students and postdoctoral researchers representing the major phase field frameworks were asked to solve these benchmark problems. This hackathon allowed for the first direct comparison of codes and the results were presented and discussed during the

CHiMaD Phase Field Methods Workshop II on October 15-16,2015. As a result of these discussions, the benchmark were improved. To continue the discussion, a third workshop is being planned for 2016, along with another hackathon.

31st Steel Research Group (SRG) Meeting
March 23-24, 2015 | Northwestern University
NU-NIMS for Materials Innovation: Joint MGI Workshop
March 25, 2015 | Northwestern University
Organizer: Gregory **Olson** (NU)

Scope Northwestern's Steel Research Group (SRG) materials design consortium joined the CHiMaD umbrella organization during Year One, offering the leveraging opportunity of the CALPHAD-based metals design projects with topics and sponsors listed in Figure 19.1.

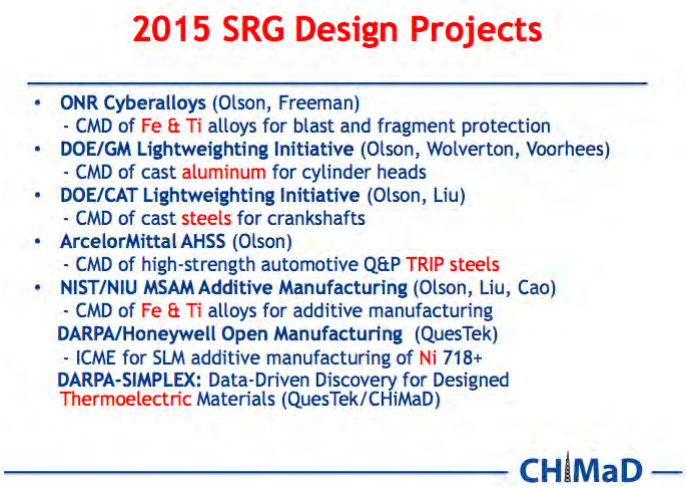


Figure 19.1: SRG Materials Design Projects

Of particular note in 2015 was the fragment penetration testing of the ONR Cyberalloys 2020 prototype austenitic blast protection TRIP steel. Under optimized transformation stability, numerous arrested shear bands were found with clear transformation zones at their tips, supporting the effectiveness of transformation plasticity in inhibiting adiabatic shear localization. The collaboration with GM under the DOE Lightweighting Initiative has quantified the thermodynamics and kinetics of Q phase precipitation strengthening in support of cast Al alloys with higher temperature performance. Caterpillar collaboration under the same DOE initiative has adapted multiphase precipitation concepts from our previous martensitic blast protection steel designs to demonstrate novel cast steel prototypes for lower cost crankshaft applications. AHSS design research supported by ArcelorMittal is quantifying the nonequilibrium thermodynamics of carbon partitioning in Quench & Partition martensite-austenite TRIP steels for high formability automotive sheet applications. In support of the new process technology of additive manufacturing, the NIST-MSAM project has quantified recrystallization behavior of Ti and steel alloys, while QuesTek's collaboration with Honeywell under the DARPA Open Manufacturing initiative is supporting AIM qualification of printed Ni superalloy components for aerospace applications. Building on our CHiMaD Year One demonstration of a hybrid approach to integrating CALPHAD with datamining techniques, QuesTek has secured a $3.6M consortium project with CHiMaD to apply this approach to integrated compound discovery and predictive microstructural design in thermoelectric materials.

These projects will help demonstrate the generality of the methods, tools, and database infrastructure of CHiMaD. The SRG Annual Meeting held each March at Northwestern

will continue to serve as a review of CHiMaD metals activities offering interaction with a broader community.

CHiMaD Annual Review Meeting

May 1, 2015 | Northwestern University

Peter Voorhees presenting the overview of CHiMaD activities for 2014

Scope The Center's 2015 Annual Meeting brought together 80 CHiMaD principal investigators and collaborators from CHiMaD's partner institutions, including ASM International, QuesTek Innovations and Fayetteville State University, as well as NIST colleagues to review the CHiMaD research and outreach activities. This meeting also acts as a platform for the CHiMaD technical advisory board to review the CHiMaD research activities and provide feedback.

CHiMaD also organized its first poster session during 2015 Annual Review Meeting giving the students and postdoctoral researchers an opportunity to explain their contributions to CHiMaD research and get feedback regarding their work directly from CHiMaD principal investigators, NIST colleagues and the Technical Advisory Board. In this poster session, 25 Posters were presented representing all use-case groups, tools and the educational outreach activities.

Roadmapping for Innovation in Sheet Metal Forming Workshop

May 4-5, 2015 | Northwestern University
Organizer: Jian **Cao** (NU)

Scope This workshop brought together a select group of key academic and industry leaders to discuss and identify critical gaps, technology advancements, and innovations that could transform sheet metal forming. The program will launch a roadmapping process to guide and stimulate action to enhance the industry and U.S. competitiveness. More information can be found at http://sheetmetal-roadmap.northwestern.edu.

NIST Diffusion/CALPHAD Data Informatics and Tools Workshop

May 14-15, 2015 | National Institute of Standards and Technology

Organizers: Carelyn Campbell (NIST)

Scope This workshop hosted a series of presentations discussing the current major data informatics efforts as well as those at NIST. A complete list of talks can be found at http://www.nist.gov/mml/msed/thermodynamics_kinetics/Diffusion-Workshop-Group.cfm

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International Workshop on Advanced Co-based Superalloys: 3.0

June 23-24, 2015 | National Institute of Standards and Technology
Organizers: Eric Lass (NIST), Steffen Neumeier (FAU Erlangen-Nurnberg, Germany), Suzana Fries (RUB, Bochum, Germany)

Scope This workshop brought together an international group of researcher focusing on Co-based superalloys for 2 days of discussions and poster session.

US-Japan Materials Genome Workshop

June 23-24, 2015 | International Congress Center "Epochal Tsukuba" (JAPAN)
Plenary speakers included: James Warren (NIST), Gregory **Olson** (NU)

Scope Structural materials play a central role in National physical infrastructure development, and both the US and Japan have concerted efforts in developing structural materials for applications in maintaining, and improving their large-scale physical infrastructure. In addition, both nations have efforts to discover, design, and deploy advanced structural materials for dynamic applications as in aerospace and power generation industries. These are major undertakings that require a concerted effort ranging from fundamental materials science research, to acquiring, curating, and maintaining high-quality data, and, ultimately, to manufacturing products that are energy efficient, environmentally sustainable, and durable. The goals of this and subsequent workshops is to bring together a diverse group of researchers from the US and Japan to discuss ways to use predictive theory and modeling, combined with machine learning, data mining, and rapid-acquisition of experimental data to produce highly efficient and low-cost manufactured products.

This workshop strives to develop a collaborative framework for complementary joint research using the materials genome and concurrent engineering paradigm to meet the development goals set by each country. To this end, a 2-day agenda with 5 plenary speakers and 30 distinguished colleagues in the field to lecture and lead 5 parallel sessions were designed. The workshop helped identify both important scientific and engineering challenges in materials topics including metals, polymer composites, and ceramics.

CHiMaD Materials Design Workshop I

September 24-25, 2015 | CHiMaD Headquarters
Organizers: Ricardo Komai (NU), Wei Xiong (NU), Begum Gulsoy (NU)

Scope This workshop was organized to further introduce Materials by Design concepts to CHiMaD graduate students and postdoctoral researchers. The goal of this two-day community-building workshop was to form a Systems Design Chart for individual CHiMaD projects. This effort was very beneficial for the students and postdocs in furthering their understanding of Materials by Design and for identifying the unique materials design goals for each use-case group and its projects. Sauza (NU), Gross (NU) and Peters (NU) assisted with this course, providing leading examples of building systems design charts for

Attendees of the CHiMaD Materials Design Workshop I

their projects. The discussions during the workshop gave rise to a possible collaboration between the Data Mining and Organic Bulk Heterogeneous Polymer Solar Cells use-case groups. The students and postdocs are expected to further improve and refine the systems design chart as their projects progress. The workshop report will be made available and a follow-up workshop is planned for 2016.

Scientific Symposium on Multivalent Interactions in Polyelectrolytes: New Physics, Biology and Materials

October 2-4, 2015 | University of Chicago

Organizers: Juan **de Pablo** (UC), Sheng-Lin Gibson (NIST), Monica **Olvera de la Cruz** (NU), Vivek Prabhu (NIST), Matthew **Tirrell** (UC)

Attendees of the Scientific Symposium on Multivalent Interactions in Polyelectrolytes

Scope This symposium explored the new physical, biological and materials science possible when highly charged macromolecules interact with multivalent species of the opposite charge. Important new structures, ranging from encapsulants to ordered block copolymer phases to stress granules in biology, result from multivalent electrostatic assembly. Major opportunities in this field include: understanding counterion condensation with multivalent ions and its role in macromolecular collapse; understanding why some polyelectrolyte complexes are solid and some are fluid; design of new self-assembled structures via electrostatic complexation; specific ion effects; understanding the structure and function of membrane-less granules and compartments in biology.

About 100 researchers attended the symposium where 40 experts from around the world gave invited presentations regarding their work in the field. Matthew **Tirrell's** accomplishments in this field were recognized with a reception and dinner during the event. This symposium was mainly organized by the members of the Soft Matter Design Based on Charge Complexation use-case group.

Advances and Challenges in Soft Matter Photovoltaic Research

Novermber 13-14, 2015 | University of Chicago
Organizers: Luping **Yu** (UC), Tobin **Marks** (NU), Lee J. Richter (NIST)

Scope The aim of this symposium was to discuss recent advances, and to define what are viewed as the grand challenges for development of organic solar cells. A central aspect of the symposium was to examine emerging tools, particularly predictive computational methods and data-base related strategies, and their role in advancing OPV science and related areas (e.g., organic electronics). This symposium also served as a platform to exchange new ideas, explore common challenges, and forge cross-disciplinary collaborations. Especially useful were the discussions of solutions to critical issues we are facing in OPV area, such as low power conversion efficiency, inadequate carrier mobility, Voc losses, long term stability, theory-guided design of materials, and charge generation dynamics, to name a few. About 40 researchers attended the symposium where 10 experts gave invited presentations. This symposium was mainly organized by the members of the Organic Bulk Heterojunction Polymer Solar Cells use-case group.

Semi-Automated Data Base Creation Course, University of Chicago

Organizers: Juan **de Pablo** (UC), Debra Audus (NIST), Ian **Foster** (UC/ANL)

Attendees of the Semi-Automated Data Base Creation Course

The organizers have developed a model for semi-automated data base creation. The

current process now involves a verification step, which was implemented by teaching an undergraduate course at the University of Chicago during which students were asked to check the relevance of automated data entries into the data base. Audus (NIST) spent three weeks at Chicago collaborating on this project and co-teaching that course. A manuscript describing this project has been submitted for publication in the Journal of Chemical Education.

19.4 Other Outreach Activities Organized by CHiMaD PIs

Workshop on Predictive Theoretical and Computational Approaches for Additive Manufacturing, Washington, DC, USA (10/7/15) *Organizing PI: Jian Cao (NU)*

Low-Dimensional Nanoelectronic Materials Use-Case Group Workshop, including a CHiMaD seminar by Davydov (NIST), Evanston, IL, USA (04/30/15) *Organizing PI: Mark Hersam (NU)*

Directed Self-Assembly Professional Intensive Course, SPIE International Meeting, San Jose, CA, USA (02/15) *Organizing PI: Juan De Pablo (UC)*

Additive Manufacturing, two junior undergraduate students participated in this project where they learned basic principles of 3D printing and took part in a workshop "3D Printing and Additive Manufacturing Science and Technology" co-hosted by the U.S. Army Research Office and the University of North Carolina. One of the students wrote a senior Research Thesis on this topic. *Organizing PI: Alexander Umatsev (FSU)*

Building the Materials Data Infrastructure: A Materials Community Planning Workshop *Organizing PI: Larry Berardinis (ASM)*

In-Process Materials Data for Modeling Workshop *Organizing PI: Larry Berardinis (ASM)*

Materials Data Analytics: A Path-Finding Workshop *Organizing PI: Larry Berardinis (ASM)*

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20. Publications

[1] Xiaolong Liu et al. "Rotationally Commensurate Growth of MoS2 on Epitaxial Graphene". In: *ACS Nano* 10.1 (2016), pages 1067–75. DOI: 10.1021/acsnano.5b06398 (cited on pages 16, 19, 21).

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21. Information Dissemination

21.1 Low-Dimensional Nanoelectronic Materials

1. **X. Ren**, L. Fang, A.K. Singh, F. Tavazza, A. Davydov, M. Kanatzidis, L. Lauhon, *Atom Probe Tomography Analysis of Doping in 2-D Materials*, MRS Fall Meeting, Boston, MA, USA (12/01/2015)
2. **M. C. Hersam**, *Solution processing and device integration of two-dimensional black phosphorus,* 228th Electrochemical Society Meeting, Phoenix, AZ, USA (10/14/15).
3. **M. C. Hersam**, *Fundamentals and applications of two-dimensional nanomaterial heterostructures,* National Academies Symposium on Novel Materials, Washington, DC, USA (10/7/15).
4. **M. C. Hersam**, *Chemically modified two-dimensional nanoelectronic heterostructures,* China Nano 2015, Beijing, China (9/3/15).
5. **M. C. Hersam**, *Integration challenges and opportunities for two-dimensional materials,* Science and Technology of Two-Dimensional Materials Workshop, Orlando, FL, USA (8/21/15).
6. **M. C. Hersam**, *Solution processing and device integration at the two-dimensional limit,* 250th American Chemical Society National Meeting, Boston, MA, USA (8/17/15).
7. **M. C. Hersam**, *Carbon and related nanomaterial heterostructure devices,* Carbonhagen Symposium on Carbon and Related Nanomaterials, Copenhagen, Denmark (8/13/15).
8. **M. C. Hersam**, *Nanomaterial heterostructures for electronic and electrochemical applications,* 8th International Conference on Materials for Advanced Technologies, Singapore (7/1/15).
9. **M. C. Hersam**, *Beyond carbon nanotube thin-film transistors: Logic circuits, memory, and heterostructures,* 16th International Conference on the Science and Application of Nanotubes, Nagoya, Japan (6/30/15).
10. **M. C. Hersam**, *Solution processing and device integration of two-dimensional black phosphorus,* 6th Graphene and 2D Materials Satellite Symposium, Nagoya, Japan (6/28/15).
11. **M. C. Hersam**, *Emerging device applications for two-dimensional nanomaterial heterostructures,* 73rd Device Research Conference, Columbus, OH, USA (6/23/15).

12. **M. C. Hersam**, *Production and application of printable carbon nanomaterial inks,* 2015 TechConnect World Innovation Conference, National Harbor, MD, USA (6/17/15).
13. **M. C. Hersam**, *Anti-ambipolar, gate-tunable p-n heterojunctions,* 227th Electrochemical Society Meeting, Chicago, IL, USA (5/25/15).
14. **M. C. Hersam**, *VLSI carbon nanotube thin-film circuits,* 227th Electrochemical Society Meeting, Chicago, IL, USA (5/25/15).
15. **M. C. Hersam**, *Ubiquitous electronics and sensors: Enabling the internet of things,* Illinois Chemical Education Foundation Scholarship Luncheon, Des Plaines, IL, USA(5/21/15).
16. **M. C. Hersam**, *Solution processing and device integration at the two-dimensional limit,* European Materials Research Society Spring Meeting, Lille, France (5/13/15).
17. **M. C. Hersam**, *Integration challenges and opportunities for two-dimensional materials,* NSF US-EU Workshop on 2D Layered Materials and Devices, Arlington, VA, USA (4/23/15).
18. **M. C. Hersam**, *Integrating carbon nanomaterials into functional heterostructure devices,* Materials Research Society Spring Meeting, San Francisco, CA, USA (4/10/15).
19. **M. C. Hersam**, *Chemically modified two-dimensional nanoelectronic heterostructures,* 249th American Chemical Society National Meeting, Denver, CO, USA (3/23/15).
20. **M. C. Hersam**, *Carbon nanomaterial heterostructure devices,* 49th American Chemical Society National Meeting, Denver, CO, USA (3/22/15).
21. **M. C. Hersam**, *Nanomaterial heterostructures for electronic and energy technologies,* Workshop on Semiconductors, Electronic Materials, Thin Film, and Photonic Materials, Tel Aviv, Israel (2/23/15).
22. **M. C. Hersam**, *Integrating monodisperse nanomaterials into heterostructure devices,* Towards Reality in Nanoscale Materials VIII Workshop, Levi, Finland (2/9/15).
23. **M. C. Hersam**, *Nanomaterial heterostructures for electronic and energy technologies,* Muju International Winter School, Muju Deogyusan Resort, Korea (1/29/15).
24. **M. C. Hersam**, *Integrating nanomaterials into heterostructure devices and systems,* National Research Council of Canada Colloquium, Ottawa, Canada (1/23/15).
25. **M. C. Hersam**, *Integrating nanomaterials into heterostructure devices and systems,* Northwestern University Department of Physics and Astronomy Colloquium, Evanston, IL, USA(1/9/15).

21.2 Data Mining

1. **L. Ward**, A. Agrawal, A. Choudhary, C. Wolverton, *General Machine-Learning-Based Framework for Predicting the Properties of Materials Using Composition.* Integrating Experiments, Simulations and Machine Learning to Accelerate Materials Innovation, MRS Fall 2015. Boston, MA, USA (12/02/15)
2. **A. Choudhary**, *Transforming Materials Design to Marketing with BIG DATA SCIENCE + SUPERCOMPUTING?*, 2015 Whitney Symposium GE Global Research, Niskayuna, NY, USA (10/12/15)
3. **A. Agrawal**, *Towards an Infrastructure for Materials Data Analytics: An Overview of Tools and Platforms for Code Development, Collaboration, and Data Analytics*, Materials Research Collaboration Environment Workshop, Dayton OH, USA

(08/13/15)

4. **L. Ward**, A. Agrawal, A. Choudhary, C. Wolverton, *Accelerating Materials Discovery with Machine Learning.* Computational Materials Chemistry, Telluride Science and Research Center, Telluride, CO, USA. (06/27/15)
5. **W. Chen**, *Design of Engineered Nano-materials Systems*, School of Civil and Environmental Engineering Seminar, The University of New South Wales, Sydney, Australia (06/11/15)
6. **W. Chen**, *Design of Complex System for the 21st Century* Industrial Engineering Seminar, University of Oklahoma, Norman, OK, USA (04/03/15)
7. **W. Chen**, *Design of Emerging Materials Systems*, Mechanical Engineering Department Seminar, Texas A&M University, College Station, TX, USA (03/25/15)
8. **A. Agrawal**, *CHiMaD Data Mining: Fatigue*, 30th Steel Research Group Meeting Northwestern University, Evanston, IL USA (03/23/15)
9. **L. Ward**, V. Hedge, A. Agrawal, A. Choudhary, C. Wolverton, *Accelerating Materials Discovery with Machine Learning.* Computational Modeling and Stochastic Methods for Materials Discovery and Properties, TMS 2015. (03/17/15)
10. **L. Ward**, A. Agrawal, A. Choudhary, C. Wolverton, *Machine Learning for Materials Discovery.* (Poster Presentation). Machine Learning for Many Particle Systems, Institute for Pure and Applied Mathematics, UCLA, CA, USA (02/23/15)
11. **L. Ward**, V. Hedge, A. Agrawal, A. Choudhary, C. Wolverton, *High-Throughput Computation and Machine Learning for Materials Discovery* (Poster Presentation). Opportunities for Materials Informatics 2015. University of Wiconsin-Madison, Madison, WI, USA (02/09/15)

21.3 In-Situ Si Composites

1. **P. W. Voorhees** *The Center for Hierarchical Materials Design: Realizing the Vision of the Materials Genome Initiative.* International Summit Forum on the Materials Genome Initiative, China-MGI-2015, Shanghai China (08/15).
2. **P. W. Voorhees** *The Center for Hierarchical Materials Design: Realizing the Vision of the Materials Genome Initiative* HERO-M meeting, Stockholm, Sweden (05/15).
3. **P. W. Voorhees** *Eutectic Solidification: from Multicomponent alloys to the Macroscale* TMS Annual Meeting, Orlando FL, USA (03/15).

21.4 Soft Matter Design Based on Charge Complexation

1. **M. Olvera de la Cruz** *All-Polymer Solar Cell Performance Optimized via Systematic Molecular Weight Tuning of both Donor and Acceptor Polymers* Advances and Challenges in Soft Photovoltaic Research, University of Chicago, Chicago, IL, USA (11/13/15)
2. **E. Luijten** *Colloidal Structures from Unexpected Interactions: From Dielectric Many-Body Effects to Non- Equilibrium Phase Behavior* Chemical Physics Seminar, California Institute of Technology, CA, USA (11/15)
3. **E. Luijten** *Exploiting multivalent interactions to create new drug and gene delivery systems* International Symposium: Multivalent Interactions in Polyelectrolytes: New Physics, Biology and Materials, Institute for Molecular Engineering, University of Chicago, Chicago, IL, USA (10/15)

4. **M. Olvera de la Cruz** *Ion clusters in neutral-charged polymer blends and copolymers* ACS National Meeting, Boston, MA, USA (09/16/15)
5. **M. Olvera de la Cruz** *Ion clusters in neutral-charged polymer blends and copolymers* Beijing Institute of Technology, Beijing, China (09/05/15)
6. **E. Luijten** *The future of biomolecular modeling: Is there still room for coarse-grained models* Midwest Computational Biomolecular Modeling Symposium, Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL, USA (09/15)
7. **J. de Pablo** American Institute of Chemical Engineering National Meeting (09/15)
8. **J. de Pablo** Frauenhofer Institute International Meeting on Computational Design of Lithographic Processes, Germany (09/15)
9. **E. Luijten** *Conformation and Diffusion of DNA-Coated Nanoparticles* Symposium: Colloid Polymer Achitectures and Mixtures, Fall Meeting of the American Chemical Society, Boston, MA, USA (08/15)
10. **E. Luijten** *Self-Assembly in Colloidal Systems: New Insights through Novel Algorithms* Colloquium, Department of Mathematics, Pennsylvania State University, State College, PA, USA (08/15)
11. **E. Luijten** *Self-Assembled Gene Carriers of DNA and Graft Copolymers* Symposium: Theory and Modeling of Nanoparticle Interactions with Biomolecules and Polymers, Fall Meeting of the American Chemical Society, Boston, MA, USA (08/15)
12. **M. Olvera de la Cruz** *Ion clusters in neutral-charged polymer blends and copolymers* 1st US-Japan Materials Genome Workshop, Japan (06/22/15)
13. **E. Luijten** *Dynamic Collective Behavior and Phase Separation of Active Colloids* Complex matter physics: Active materials, dynamics and patterns, Havana, Cuba (06/15)
14. **J. de Pablo** International Symposium on Self Assembly, Taipei, Taiwan (06/15)
15. **E. Luijten** *Colloidal Structures from Unexpected Interactions: From Dielectric Many-Body Effects to Non- Equilibrium Phase Behavior* Theoretical Chemistry Seminar, Department of Chemistry, Cambridge University, U.K (05/15)
16. **E. Luijten** *Geometric Cluster Algorithm for Anisotropic Particles* Theory & Simulation Seminar, Department of Physics and Astronomy, Utrecht University, The Netherlands, (05/15)
17. **M. Olvera de la Cruz** *Ion clusters in neutral-charged polymer blends and copolymers* Penn State University, State College, PA, USA (04/21/15)
18. **E. Luijten** *New Insights into Some Principles of Self-Assembly* Keynote address: Theory and Principles of Self-Assembly, 12th Annual Conference on the Foundations of Nanoscience (FNANO15), Snowmass, Utah, USA (04/15)
19. **J. de Pablo** Materials Research Society National Meeting, (04/15)
20. **J. Zwanikken**, M. Olvera de la Cruz *Tuning the phase diagram of polyelectrolyte blends with a pinch of salt* APS Spring Meeting, San Antonio, TX, USA (03/3/15)
21. **H-K. Kwon**, M. Olvera de la Cruz *Formation of ion clusters in the phase separated structures of neutral-charged polymer blends* APS Spring Meeting, San Antonio, TX, USA (03/3/15)
22. **E. Luijten** *Patchy Colloids: Collective behavior of Janus particles* Three-hour lecture series at Geilo School on Cooperative particles: Patchy colloids, active matter and nanofluids, Institute for Energy Technology, Geilo, Norway (03/15)
23. **J. de Pablo** American Chemical Society National Meeting, San Diego, CA, USA (03/15)

24. **J. de Pablo** American Physical Society National Meeting, Baltimore, MD, USA (03/15)
25. **E. Luijten** *Colloidal Self-Assembly Controlled by Dielectric Many-Body Effects* Nano Seminar,Debye Institute, Utrecht University, The Netherlands, (02/15)
26. **E. Luijten** *Accelerated Monte Carlo Methods for Computational Materials Science* CIERA (Center for Interdisciplinary Exploration and Research in Astrophysics), Northwestern University, (02/15)
27. **J. de Pablo** SPIE International Lithography Meeting, San Jose, CA, USA (02/15)
28. **J. de Pablo** Photopolymer International Conference, Chiba, Japan, 2015

21.5 Directed Self-Assembly of Block Copolymers for Lithography

1. **H. Jaeger** IME Industrial Affiliates Meeting, University of Chicago, Chicago, IL, USA (11/12/15)
2. **H. Jaeger** plenary lecture at Particles 2015, Barcelona, Spain (10/29/15)
3. **J. de Pablo** American Institute of Chemical Engineering National Meeting (09/15)
4. **J. de Pablo** Frauenhofer Institute International Meeting on Computational Design of Lithographic Processes, Germany (09/15)
5. **H. Jaeger** Designer Matter Workshop, AMOLF, Amsterdam, The Netherlands (06/33/15)
6. **J. de Pablo** International Symposium on Self Assembly, Taipei, Taiwan (06/15)
7. **J. Raybin**, S. Sibener Chemical and Biological Defense Science & Technology Conference, St. Louis, MO, USA (05/12/15)
8. **H. Jaeger** Active Matter Summit, MIT, Boston, MA, USA (04/25/15)
9. **J. de Pablo** Materials Research Society National Meeting, (04/15)
10. **J. de Pablo** American Chemical Society National Meeting, San Diego, CA, USA (03/15)
11. **H. Jaeger** APS March Meeting, San Antonio, TX, USA (03/03/15)
12. **J. de Pablo** American Physical Society National Meeting, Baltimore, MD, USA (03/15)
13. **J. de Pablo** *Directed self-assembly at molecular length scales and the interplay between experiment, theory, and simulation* SPIE International Lithography Meeting, San Jose, CA, USA (02/24/15)
14. **H. Jaeger** Plenary Lecture, Annual meeting of Dutch Physical Society, Veldhoven, The Netherlands (01/20/15)
15. **J. de Pablo** Photopolymer International Conference, Chiba, Japan, 2015

21.6 Polymer Matrix Materials

1. **E. Luijten** *Colloidal Structures from Unexpected Interactions: From Dielectric Many-Body Effects to Non- Equilibrium Phase Behavior* Chemical Physics Seminar, California Institute of Technology, CA, USA (11/15)
2. **S. Keten**, *Invited Talk*, MRS Fall Meeting, Boston, MA, USA (11/15)
3. **E. Luijten** *Exploiting multivalent interactions to create new drug and gene delivery systems* International Symposium: Multivalent Interactions in Polyelectrolytes: New Physics, Biology and Materials, Institute for Molecular Engineering, University of Chicago, Chicago, IL, USA (10/15)

4. **E. Luijten** *The future of biomolecular modeling: Is there still room for coarse-grained models* Midwest Computational Biomolecular Modeling Symposium, Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL, USA (09/15)
5. **J. de Pablo** American Institute of Chemical Engineering National Meeting (09/15)
6. **J. de Pablo** Frauenhofer Institute International Meeting on Computational Design of Lithographic Processes, Germany (09/15)
7. **E. Luijten** *Conformation and Diffusion of DNA-Coated Nanoparticles* Symposium: Colloid Polymer Achitectures and Mixtures, Fall Meeting of the American Chemical Society, Boston, MA, USA (08/15)
8. **E. Luijten** *Self-Assembly in Colloidal Systems: New Insights through Novel Algorithms* Colloquium, Department of Mathematics, Pennsylvania State University, State College, PA, USA (08/15)
9. **E. Luijten** *Self-Assembled Gene Carriers of DNA and Graft Copolymers* Symposium: Theory and Modeling of Nanoparticle Interactions with Biomolecules and Polymers, Fall Meeting of the American Chemical Society, Boston, MA, USA (08/15)
10. **S. Keten**, *Mesoscale Modeling of the Interfacial Mechanics of Nanocellulose Composites*, 2015 TAPPI International Conference on Nanotechnology for Renewable Materials, Atlanta, GA, USA (06/24/15)
11. **S. Keten**, *Discerning Nanoconfinement Effects in Bioinspired Nanocomposites Through Predictive Multi-scale Simulations*, ASCE Engineering Mechanics Institute Conference, Standford, CA, USA (06/17/15)
12. **W. Chen**, *Design of Engineered Nano-materials Systems*, School of Civil and Environmental Engineering Seminar, The University of New South Wales, Sydney, Australia (06/11/15)
13. **E. Luijten** *Dynamic Collective Behavior and Phase Separation of Active Colloids* Complex matter physics: Active materials, dynamics and patterns, Havana, Cuba, (06/15)
14. **J. de Pablo** International Symposium on Self Assembly, Taipei, Taiwan (06/15)
15. **E. Luijten** *Colloidal Structures from Unexpected Interactions: From Dielectric Many-Body Effects to Non- Equilibrium Phase Behavior* Theoretical Chemistry Seminar, Department of Chemistry, Cambridge University, U.K (05/15)
16. **E. Luijten** *Geometric Cluster Algorithm for Anisotropic Particles* Theory & Simulation Seminar, Department of Physics and Astronomy, Utrecht University, The Netherlands, (05/15)
17. **W. Chen**, *Design of Complex System for the 21st Century* Industrial Engineering Seminar, University of Oklahoma, Norman, OK, USA (04/03/15)
18. **E. Luijten** *New Insights into Some Principles of Self-Assembly* Keynote address: Theory and Principles of Self-Assembly, 12th Annual Conference on the Foundations of Nanoscience (FNANO15), Snowmass, Utah, USA (04/15)
19. **J. de Pablo** Materials Research Society National Meeting (04/15)
20. **W. Chen**, *Design of Emerging Materials Systems*, Mechanical Engineering Department Seminar, Texas A&M University, College Station, TX, USA (03/25/15)
21. **S. Keten**, *Stick-slip Shear Phenomenon of Interfaces Between Cellulose Nanocrystals*, American Chemical Society National Meeting & Exposition, Denver, CO, USA (03/22/15)
22. **E. Luijten** *Patchy Colloids: Collective behavior of Janus particles* Three-hour lecture series at Geilo School on Cooperative particles: Patchy colloids, active matter

and nanofluids, Institute for Energy Technology, Geilo, Norway (03/15)

23. **E. Luijten** *Colloidal Self-Assembly Controlled by Dielectric Many-Body Effects* Nano Seminar,Debye Institute, Utrecht University, The Netherlands (02/15)
24. **E. Luijten** *Accelerated Monte Carlo Methods for Computational Materials Science* CIERA (Center for Interdisciplinary Exploration and Research in Astrophysics), Northwestern University, Evanston, IL, USA (02/15)
25. **J. de Pablo** American Chemical Society National Meeting, San Diego, CA, USA (03/15)
26. **J. de Pablo** American Physical Society National Meeting, Baltimore, MD, USA (03/15)
27. **S. Keten**, *Department Seminar*, MIT, Boston, MA, USA (2015)
28. **S. Keten**, *Department Seminar*, Brown University, Providence, RI, USA (2015)
29. **S. Keten**, *Department Seminar*, Columbia University, New York, NY, USA (2015)
30. **S. Keten**, *Seminar*, SES Conference, (2015)
31. **S. Keten**, *Seminar*, Dow Chemical Company (2015)
32. **J. de Pablo** Photopolymer International Conference, Chiba, Japan, 2015

21.7 Precipitation-Strengthened Alloys

1. **D. Sauza**, P. Boccini, D. Dunand, D. Seidman *Microstructure and Mechanical Properties of novel γ'-strengthened Co-based Superalloys* Alcoa Technical Center, Pittsburgh, PA, USA (07/30/15)
2. **A. Umanstev** *Formation of Amorphous Nanophases*, International Conference on Solid-Solid Phase Transformations in Inorganic Materials (PTM 2015), Whistler, CANADA (06/28/15)
3. **A. Umantsev** *Nucleation at Large Driving Forces*, Workshop for Theorists at Undergraduate Institutions, Kavli Institute for Theoretical Physics, UCSB, Santa Barbara CA, USA (06/22/15)
4. **W. Chen** *Design of Engineered Nano-materials Systems*, Seminar, School of Civil and Environmental Engineering, The University of New South Wales, Newport, UK (06/11/15)
5. **D. Seidman**, P. Bocchini, D. Sauza, D. Dunand, *Co-based superalloys with γ(f.c.c.) plus γ' (L12) microstructure*, NIST, Gaithersburg, MD, USA (06/05/2015)
6. **D. Dunand** *Novel Cobalt-based Superalloys*, Briefing to Shanghai Jiao Tong University delegation, Northwestern University, Evanston, IL, USA (04/07/15)
7. **D. Dunand** *Novel Cobalt-based Superalloys*, Department Seminar, Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA, USA (04/07/15)
8. **W. Chen** *Design of Complex System for the 21st Century*, Invited Seminar, Industrial Engineering, University of Oklahoma, Norman, OK, USA (04/03/15)
9. **W. Chen** *Design of Emerging Materials Systems*, Department Seminar, Mechanical Engineering, Texas A&M University, College Station, TX, USA (03/25/15)
10. **A. Umantsev** *Long-Period Stacking Fault Structures of Magnesium-Base Alloys*, Keynote, International Conference PLASTICITY 2015, Montego Bay, Jamaica (01/06/15)

21.8 Organic Bulk Heterojunction Polymer Solar Cells

1. **M. Goldey**, G. Galli *Electronic Structure Properties as Signatures of Morphological Motifs in Organic Photovoltaics* Advances and Challenges in Soft Matter Photovoltaic Research, University of Chicago, Chicago, IL, USA (11/13/15)
2. **M. Goldey**, G. Galli *Organic Solar Cell Models Predict How Structures Change Properties* Mindbytes Research Computing Expo, University of Chicago, Chicago, IL, USA (10/27/15)
3. **L.Yu**, Department Seminar, Macromolecules Science and Engineering Institute, University of Michigan, Ann Arbor, MI, USA (10/12/15)
4. **M. Goldey**, G. Galli *First Principles Simulations of Organic Solar Cells* Argonne Postdoctoral Research and Career Symposium, Argonne National Laboratory, Lemont, IL, USA (10/08/15)
5. **M. Goldey**, **A. Scheneider** *Organic Bulk Heterojunction Polymer Solar Cells Materials Design* CHiMaD Materials Design Workshop, CHiMaD Headquarters, Evanston, IL, USA (09/25/15)
6. **J. de Pablo** American Institute of Chemical Engineering National Meeting (09/15)
7. **J. de Pablo** Frauenhofer Institute International Meeting on Computational Design of Lithographic Processes, Germany (09/15)
8. **L.Yu**, Plenary Talk, Organic solid state electronics, Beijing, China (08/08/15)
9. **J. de Pablo** International Symposium on Self Assembly, Taipei, Taiwan (06/15)
10. **J. de Pablo** Materials Research Society National Meeting (04/15)
11. **J. de Pablo** American Chemical Society National Meeting, San Diego, CA, USA (03/15)
12. **J. de Pablo** American Physical Society National Meeting, Baltimore, MD, USA (03/15)
13. **J. de Pablo** Photopolymer International Conference, Chiba, Japan, 2015

21.9 Materials Data Facility

1. **B. Blaiszik**, K. Chard, I. Foster. *The Materials Data Facility (MDF): Data Services to Advance Materials Research*, Integrated Imaging Initiative Seminar, Argonne National Laboratory, Lemont, IL, USA (12/15)
2. **B. Blaiszik**, K. Chard, I. Foster. *The Materials Data Facility (MDF): Data Services to Advance Materials Research*, National Center for Supercomputing Applications Joint Materials Science Seminar, University of Illinois at Urbana-Champaign, Urbana, IL, USA (12/15)
3. **I. Foster**, B. Blaiszik, K. Chard. *The Materials Data Facility*, 4th National Data Service Consortium Workshop, San Diego, CA, USA (10/15)
4. **B. Blaiszik**, K. Chard, J. Pruyne, J. Towns, S. Tuecke, I. Foster. *The Materials Data Facility (MDF): Data Services to Advance Materials Research*, Materials Science and Technology Conference, Columbus, OH, USA (10/15)
5. **B. Blaiszik**, K. Chard, R. Ananthakrishnan, J. Pruyne, J. Wozniak, M. Wilde, R. Osborn, S. Tuecke, I. Foster. *Globus Research Data Management Services and the Materials Data Facility*, Center for PRedictive Integrated Structural Materials Science (PRISMS) Annual Meeting, Ann Harbor, MI, USA (09/15)

21.10 Additive Manufacturing

1. J. Cao *Additive Manufacturing* Predictive Theoretical and Computational Approaches for Additive Manufacturing Workshop by U.S. National Committee on Theoretical and Applied Mechanics (USNC/TAM), Washington, D.C, USA (10/7/15)
2. J. Bennett *Introduction to Predictive Theoretical and Computational Approaches to Additive Manufacturing* Instructor, Predictive Theoretical and Computational Approaches to Additive Manufacturing Workshop, 13th Annual US National Congress on Computational Mechanics, San Diego, CA (07/26/15)

21.11 Coarse Grained Simulations of Organic Polymer Solar Cells

1. **M. Olvera de la Cruz** *All-Polymer Solar Cell Performance Optimized via Systematic Molecular Weight Tuning of both Donor and Acceptor Polymers* Advances and Challenges in Soft Photovoltaic Research, University of Chicago, Chicago, IL, USA (11/13/15)
2. **M. Olvera de la Cruz** *Ion clusters in neutral-charged polymer blends and copolymers* ACS National Meeting, Boston, MA, USA (09/16/15)
3. **M. Olvera de la Cruz** *Ion clusters in neutral-charged polymer blends and copolymers* Beijing Institute of Technology, Beijing, China (09/05/15)
4. **M. Olvera de la Cruz** *Ion clusters in neutral-charged polymer blends and copolymers* 1st US-Japan Materials Genome Workshop, Japan (06/22/15)
5. **M. Olvera de la Cruz** *Ion clusters in neutral-charged polymer blends and copolymers* Penn State University, State College, PA, USA (04/21/15)

21.12 Phase Field Methods

1. D. Chopp *The Locally Adaptive Time Stepping (LATS) Method: From Hodgkin-Huxley to Cahn-Hilliard* Applied Math Colloquium, University of Washington, Seattle, WA (04/29/15)
2. O. Heinonen *Length Scale Bridges* Seminar, Los Alamos National Laboratory, Los Alamos, NM, USA (04/23/15)
3. O. Heinonen *Coupling Molecular Dynamics and First-principle Electronic Structure Modeling of Disordered Heterostructures* Invited presentation, "High Performance and Parallel Computing for Materials Defects and Multiphase Flows" Workshop, National University of Singapore, Singapore (01/15/15)

21.13 ASM Educational Outreach

1. L. Berardinis *Materials Data Infrastructure Development Efforts: Update and Forecast* Materials Science & Technology Conference (MS&T 2015), Columbus , OH, USA (10/04/15)
2. L. Berardinis *Innovation Showcase* Digital Manufacturing and Design Innovation Institute Project Call Workshop (DMDII-15-11 Completing the Model-Based Definition), Chicago, IL, USA (09/10/15)
3. L. Berardinis *CMD Network: Working for the Materials Data Community* Materials Research Collaboration Environment Workshop, Dayton, OH, USA (08/13/15)

4. L. Berardinis *A Review of Materials Data Infrastructure Projects* 3rd World Congress on Integrated Computational Materials Engineering (ICME 2015), Colorado Springs, CO, USA (05/31/15)
5. L. Berardinis *ASM announces winners of Materials Genome Toolkit Competition* CMD Network e-newsletter Articles (03/14/15)
6. L. Berardinis *CHiMaD Consortium Releases First Annual Report* CMD Network e-newsletter Articles (03/14/15)
7. L. Berardinis *Materials Genome Initiative* Poster Presentation, 6th North American Materials Education Symposium, Columbus , OH, USA (03/26/15)
8. L. Berardinis *Judging set to begin on ASM Materials Genome Toolkit Competition* CMD Network e-newsletter Articles (03/12/15)
9. L. Berardinis *Inventory of Materials Data Infrastructure Development Projects and Related Initiatives* Building the Materials Data Infrastructure: A Materials Community Planning Workshop, Arlington, VA, USA (01/21/15)

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