Workshop on Coarse-Grained Modeling of Polymers and Soft Materials for the Materials Genome Initiative

August 6-7, 2014

National Institute of Standards and Technology (NIST)
Gaithersburg, MD

Sponsored by

- Material Measurement Laboratory (MML), NIST
- Center for Hierarchical Materials Design (CHiMaD)

Organizing Committee

- Juan de Pablo, University Chicago/CHiMaD
- Jack F. Douglas, NIST
- Frederick R. Phelan Jr., NIST
- Rob Riggleman, University of Pennsylvania

Workshop on Coarse-Grained Modeling of Polymers and Soft Materials for the Materials Genome Initiative

Description

Theme: Quantitative Multi-Scale Modeling for the Materials Genome Initiative

The grand challenge of the Materials Genome Initiative is the development of a national infrastructure for data sharing and analysis to support the emerging multiscale modeling paradigm of Integrated Computational Materials Engineering (ICME). To meet this challenge, techniques, tools and standards for the representation and interoperability of materials data and the interoperation of modeling systems at multiple length and time scales must be developed. This is especially necessary for polymers and related soft materials. For these systems, atomistic simulations are often limited in their ability to model their dynamics over the full range of length and time scales necessary to describe their properties. This limitation is in great part due to the divergence between the time scales for thermal vibrations of individual atoms and the chain-scale relaxation of individual polymers with increasing molecular weight and architectural complexity, but also due to practical limitations in computational resources needed to describe large scale atomistic features. Recognition of this has led to the development of a variety of coarse-graining techniques, each formulated to address problems inherent to particular scales. In this workshop, we propose to examine some of the best coarse-grained models presently available across a wide spectrum of length and time scales with a two-fold goal. The first being to discuss what is needed to improve the state of the art on current models; and second, to discuss how a common framework for connecting models between different scales can be developed. There will also be discussion on at least one special topic -- the necessity of a "CALPHAD for Polymers" approach to meet the goals of the MGI -- as well as any other major topics deemed relevant by the participants.

Workshop on Coarse-Grained Modeling of Polymers and Soft Materials for the Materials Genome Initiative

Invited Speakers

Sessions have been structured to coordinate discussion on models across increasingly larger length and time scales and will be capped with open discussion periods.

Session I: Developments in Quantitative Coarse-Graining and Bottom-Up Methods

- Will Noid, Penn State
- Roland Faller, University of California at Davis
- Pieter in 't Veld, BASF
- Sergey Izvekov, ARL

Session II: Mesoscale Modeling, Material Properties and Non-Equilibrium Dynamics

- Marina Guenza, University of Oregon
- Jay Schieber, Illinois Institute of Technology
- Mark Robbins, Johns Hopkins University
- Marcus Müller, University of Göttingen

Session III: Scale-Bridging, Mesoscale Continuum Models and Applications

- Venkat Ganesan, University of Texas at Austin
- James Elliott, University of Cambridge
- Monica Olvera de la Cruz, Northwestern University
- Laszlo Granasy, Hungarian Academy of Sciences

Session IV: Plotting the Path Forward

- Opportunities for Scale Linking in Multiscale Modeling
- Discussion of CALPHAD for Polymers Approach
- High Level Data Containers and Data Mining

Program Schedule – Day 1

Wednesday August 6, 2014
Green Auditorium

9:00 AM	Welcome and Introductions	Fred Phelan, NIST James Warren, NIST Juan de Pablo, CHiMaD
	Session I: Developments in Quantitative Coarse-Graining and Bottom-Up Methods	Moderator: Fred Phelan
9:25 AM	Announcements and Session Introduction	
9:30 AM	Challenges for Coarse-Graining the Structure And Thermodynamics of Soft Materials	Will Noid, Penn State
10:00 AM	Structural Coarse-Graining for Polymers Under Different Conditions - Opportunities and Limitations	Roland Faller, UC Davis
10:30 AM	*Coffee Break (30 minutes)*	
11:00 AM	Driving Innovation for Advanced Materials & Systems Soft Matter Modeling	Pieter in 't Veld, BASF
11:30 AM	Multi-Scale Coarse-Graining of Non-Conservative Interactions in Molecular Systems and its Application to Coarse-Graining of Molecular Explosives	Sergei Izvekov, ARL
12:00 PM	Discussion Session I	
12:30 PM	*Lunch (70 minutes)*	NIST Cafeteria
	Session II: Mesoscale Modeling, Material Properties and Non-Equilibrium Dynamics	Moderator: Rob Riggleman
1:40 PM	Announcements and Session Introduction	
1:45 PM	A Coarse-Graining Method that Preserves the Free Energy, Structural Correlations, and Thermodynamic State of Polymer Melts From the Atomistic to the Mesoscale	Marina Guenza, Oregon
2:15 PM	Nonlinear Rheology Predictions of Highly Entangled Polymers from Coarse-Graining Atomistic Simulations	Jay Schieber, IIT
2:45 PM	*Coffee Break (45 minutes)*	
3:30 PM	Mechanical Properties of Glassy Polymers from Coarse-Grained Simulations	Mark Robbins, Johns-Hopkins
4:00 PM	Simulating Morphology Transitions in Block Copolymer Materials	Marcus Müller, Göttingen
4:30 PM	Discussion Session II	
5:00 PM	Day 1 Adjournment – Announcements and Travel Logistics	
6:30 PM	Dinner(Cash)	That’s Amore!, Gaithersburg

Program Schedule – Day 2

Thursday, August 7, 2014
Green Auditorium

	Session III: Scale-Bridging, Mesoscale Continuum Models and Applications	Moderator: Jack Douglas
8:55 AM	Announcements and Session Introduction	
9:00 AM	Equilibrium and dynamical coarse-graining of polymer nanoparticle mixtures	Venkat Ganesan, UT Austin
9:30 AM	Polymeric and Composite Electrolyte Membranes: Insights from Multiscale Modeling	James Elliott, Cambridge
10:00 AM	*Coffee Break (30 minutes)*	
10:30 AM	Ionic Bilayers Tail Packing and Mesoscale Geometry	Monica Olvera de la Cruz, Northwestern
11:00 AM	Phase-Field Modeling of Polycrystalline Solidification: From Needle Crystals to Spherulites	Laszlo Granasy, Wigner Research Centre for Physics
11:30 AM	Discussion Session III	
12:00 PM	*Lunch (1 hour)*	NIST Cafeteria
1:00 PM	Session IV: Plotting the Path Forward - Opportunities for Scale Linking - Discussion of CALPHAD for Polymers Approach - High Level Data Containers and Data Mining	Moderator: Juan de Pablo
2:00 PM	Adjournment	

Session I: Developments in Quantitative Coarse-Graining and Bottom-Up Methods

Challenges for coarse-graining the structure and thermodynamics of soft materials

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University Park, PA, USA

ABSTRACT

Low resolution coarse-grained (CG) models are widely adopted for investigating soft materials. Nevertheless, it remains challenging to determine CG models that accurately describe both structure and thermodynamic properties. In this talk, we discuss a variational method for determining accurate models directly from structural information via a generalized-Yvon-Born-Green (g-YBG) theory that is exact in principle and provides accurate models for many complex systems in practice. In particular, we demonstrate a very coarse, but quite accurate, g-YBG model for the structure of PEO ionomers. Quite generally, the accuracy of CG models depends upon the representation of the system. Accordingly, we investigate the impact of the model representation upon the structural and thermodynamic properties of CG models. Finally, as time permits, we present a framework for systematically improving the transferability of CG models.

Session I: Developments in Quantitative Coarse-Graining and Bottom-Up Methods

Structural coarse-graining for polymers under different conditions - Opportunities and limitations

Roland Faller
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University of California at Davis
Davis, California, USA

ABSTRACT

This talk will focus on developing and applying structural coarse-graining techniques for polymers in condensed phases as a function of conditions. Especially the Iterative Boltzmann Inversion (IBI) technique has attracted a lot of interested over recent years. The fundamentals of the technique and expansions for heterogeneous systems including polymer blends, solutions and systems under confinement will be discussed. This includes exploring the limits of IBI in confined systems using the example of polystyrene solutions. In general the transferability between different degrees of confinement is examined as well as transferability of potentials between conditions in general.

We then apply the IBI to a system for polymer-based solar cells where we focus on the photo-active layer which contains a bicontinuous percolating network called a bulk heterojunction (BHJ). Prediction of the active-layer microstructure based on the constituent electron-donor and electron-acceptor phases and the processing conditions remains challenging. Atomistic computer simulations are only feasible to studying systems not much larger than an exciton diffusion length. Therefore we use IBI for the widely used conducting polymer poly(3-hexylthiophene) (P3HT) and various fullerenes to characterize the structure and dynamic evolution of the BHJ microstructure as a function of polymer:fullerene mole fraction and polymer chain length for systems approaching the scale of photovoltaic devices. We also will present recent work on applying the technique to a number of different biopolymers.

Session I: Developments in Quantitative Coarse-Graining and Bottom-Up Methods

Driving innovation for advanced materials & systems soft matter modeling

Pieter J. in 't Veld,
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BASF SE, Ludwigshafen, Germany

ABSTRACT

BASF is a multi-billion dollar company active in creating chemical solutions for a wide range of applications, such as home and personal care, printing and packaging, automotive and structural coatings, and structural plastics and foams applications. Within the scope of my presentation, I intend to present typical modeling work within the GM division, which focuses on Material Systems. These Material Systems vary from dispersions to filled polymeric foams. The modeling work touched includes an in-house development of an initial structure generator for particle simulations. This structure generator functions as a central piece of our approach to particle simulations, which ranges from atomistic to highly coarse-grained simulations. As an example of our standard work flow, I will show a few applications, which include the design of a stabilizer molecule for dispersing polymer particles and the simulation of polystyrene dispersions.

Session I: Developments in Quantitative Coarse-Graining and Bottom-Up Methods

Multi-scale coarse-graining of non-conservative interactions in molecular systems and its application to coarse-graining of molecular explosives

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ABSTRACT

We present an efficient bottom-up methodology for constructing non-conservative (friction and stochastic) interactions for dissipative particle dynamics (DPD) models.[1] The distance dependent radial and shear frictions and stochastic interactions in functional-free form are derived consistently with a chosen form for conservative interactions by matching two-body force-velocity and three-body velocity-velocity correlations along the microscopic trajectories of the centroids of Voronoi cells, which represent the dissipative coarse-grained particles within the DPD description. Consistently with a notion of many-body DPD, the conservative interactions are determined through the multi-scale coarse-graining (MS-CG) method, which naturally implements a pairwise decomposition of the microscopic free energy. The new method is applied to perform hierarchical coarse-graining of two common molecular explosives: nitromethane (NM) and cyclotrimethylenetrinitramine (RDX). The framework presented herein can be used to develop computational models of complex molecular materials which are capable of bridging the atomistic and mesoscopic scales.

References:
[1] S. Izvekov and B. M. Rice, J. Chem. Phys. 140 (10), 104104 (2014).

Session II: Mesoscale Modeling, Material Properties and Non-Equilibrium Dynamics

A coarse-graining method that preserves the free energy, structural correlations, and thermodynamic state of polymer melts from the atomistic to the mesoscale

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ABSTRACT

Based on the solution of the Ornstein-Zernike Equation, we present our coarse-graining method that is structural and thermodynamic consistent across multiple length scales.[1] The model is analytical and depends on molecular and thermodynamic parameters of the system under study, as well as on the direct correlation function in the k -->0 limit, c_0.[2] This single non-trivial quantity parameterizes the coarse-grained potential, and its value can be obtained numerically from the PRISM integral equation, or directly from the experimental compressibility of the system.
Direct comparison with united atom simulations of both the analytical equations and mesoscale simulations shows quantitative consistency of structural and thermodynamic properties independent of the chosen level of representation.[3] The model in this way is fully predictive, when the potential is used as an input in mesoscale molecular dynamic simulations of polymer melts.

References
[1] A. J. Clark, J. McCarty, I. Y. Lyubimov, and M. G. Guenza Phys. Rev. Lett. 109, 168301 (2012).
[2] A. J. Clark, J. McCarty, and M. G. Guenza J. Chem. Phys. 139, 124906 (2013).
[3] J. McCarty, A. J. Clark, J. Copperman, and M. G. Guenza J. Chem. Phys. 140, 204913 (2014).

Session II: Mesoscale Modeling, Material Properties and Non-Equilibrium Dynamics

Nonlinear rheology predictions of highly entangled polymers from coarse-graining atomistic simulations

Marat Andreev, Rudi Steenbakkers, and Jay D. Schieber*
Center for Molecular Study of Condensed Soft Matter (μCoSM)
Illinois Institute of Technology
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ABSTRACT

We use a slip-link picture for entangled homopolymers to derive a set of integrated, well-defined mathematical models on varying levels of description. Each level is applicable to any chain architecture, molecular weight, or blend, and under any flow. For an atomistic basis we exploit primitive-path analysis to find the statistics of topological constraints. These statistics determine all but a single (monomeric friction) parameter in our most-detailed slip-link model. We then go through a series of coarse-graining steps to create a hierarchy of integrated slip-link models. This procedure produces a mathematical model whose calculations are 3 million times faster than the most-detailed level of description, and 20 billion times faster than atomistic-level calculations. Using any single member of the hierarchy, we can then fit our friction parameter to a dynamic equilibrium experiment of a single chain molecular weight and architecture, and make predictions of the non-linear rheology of any chain architecture, molecular weight, blends of these and in any flow field. Predictions of experiment are quantitative. Porting of our code to GPUs gives an additional speed up of 200 times, or a total of 7×1013 over MD, making most calculations possible on a desktop computer with a single graphics card. More important than computational speed up is the dramatic reduction in the number of dynamic variables necessary to describe the system, which suggests a deep understanding of the physics of entangled polymers, justifying the postulations made by Sam Edwards and Pierre-Gilles de Gennes more than 40 years ago. Given that the time scales of the adjusted friction are order nanoseconds, truly ab initio rheology predictions of entangled homopolymers now seem possible.

Session II: Mesoscale Modeling, Material Properties and Non-Equilibrium Dynamics

Mechanical properties of glassy polymers from coarse-grained simulations

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Session II: Mesoscale Modeling, Material Properties and Non-Equilibrium Dynamics

Simulating morphology transitions in block copolymer materials

Marcus Müller
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ABSTRACT

The free-energy landscape of self-assembling block copolymer systems is characterized by a multitude of metastable minima and concomitant protracted relaxation times of the morphology. Using only the minimal set of relevant interactions whose strength is related to experimentally measurable quantities (top-down approach), soft coarse-grained models can access the large time and length scales that characterize the collective change of the morphology. We study the kinetics of self-assembly and the minimum free-energy path of morphology transitions by computer simulation and self-consistent field theory. Two examples will be discussed:
a) Tailoring the kinetics of structure formation in block copolymers, we propose to reproducibly direct the self-assembly of block copolymers such that the system becomes trapped in a desired long-lived metastable morphology. To this end, it is necessary to (i) control the generation of well-defined, highly unstable states and (ii) design the unstable state such that the ensuing spontaneous kinetics of structure formation reaches the desired metastable morphology. This process-directed self-assembly provides an alternative to fine-tuning molecular architecture by synthesis or blending in order to fabricate complex network structures. Comparing our simulation results to recently developed free-energy techniques, we critically assess their ability to predict spontaneous formation and highlight the importance of non-equilibrium molecular conformations in the starting state and the local conservation of density.
b) Directed self-assembly (DSA) of block copolymer films on chemically patterned substrates is a promising strategy for generating defect-free and registered structures at the nanoscale. Defects are formed during the kinetics of structure formation and are metastable. Using particle simulations and self-consistent field theory we study defect removal from a thin block copolymer film. We explore process conditions, under which defect formation is suppressed and defect removal is accelerated. Several reasons why defect-free assembly is obtained in the vicinity of the order-disorder transition are discussed.

Session III: Scale-Bridging, Mesoscale Continuum Models and Applications

Equilibrium and dynamical coarse-graining of polymer nanoparticle mixtures

Venkat Ganesan
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ABSTRACT

This talk will discuss our recent efforts in the development of a coarse-graining approach capable of capturing the equilibrium and dynamical properties of polymer nanoparticle mixtures. We first demonstrate that even at low particle volume fractions, the polymer-mediated many-body interaction effects can prove significant in determining the structural characteristics of mixtures of nanoparticles and polymer melts. To account for such effects, we propose a new simulation approach which employs a coarse-grained representation of the polymers to capture the many-body corrections to the polymer-mediated pair interaction potentials. The results of the coarse-grained simulations are shown to be in good quantitative agreement with the reference simulations. If there is time, in the second part of the talk, we demonstrate a method which extends our equilibrium coarse-graining scheme to account for the dynamical effects. Preliminary results are used to suggest that the latter allows us to capture the rheological properties of the nanocomposites.

Session III: Scale-Bridging, Mesoscale Continuum Models and Applications

Polymeric and composite electrolyte membranes: Insights from multiscale modeling

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ABSTRACT

Perfluorosulfonic acid (PFSA) electrolyte membranes, such as Nafion, are widely employed in fuel cells due to their high proton conductivity combined with excellent chemical and thermal stability. However, the very high degree of disorder in these materials makes it difficult, if not impossible, to deduce their bulk morphology unambiguously from experiments alone without the aid of computational modeling over multiple time and length scales, from the molecular [1] to mesoscale [2].
A further complication in the composite membrane-electrode assemblies (MEAs) is the presence of complex multiphase interfaces between the polymer, catalyst and carbon electrode. In this presentation, I will describe a recent combination of a model-independent procedure for obtaining structural information from small angle scattering based on a Maximum Entropy (MaxEnt) approach coupled with mesoscale simulations using Dissipative Particle Dynamics (DPD) of the morphology of Nafion parameterized with atomistic calculations and density functional theory [3].
These two methods show that the nanoscale ionic clustering in PFSAs is composed of a bicontinuous network of ionic clusters embedded in a matrix of fluorocarbon chains. I will also present results from composite systems in which the distribution of water and ionic groups at the interface in nanoscopic channels are compared with those in bulk membrane. The results show that the structure of thin (5-10 nm) layers of PFSA membranes is quite different to that in bulk, and may play a key role in controlling performance of MEAs.

[1] J.A. Elliott and S.J. Paddison Phys. Chem. Chem. Phys., 9, 2602-2618 (2007).
[2] D.S. Wu, S.J. Paddison and J.A. Elliott Macromolecules, 42, 3358-3367 (2009).
[3] J.A. Elliott, D. Wu, S.J. Paddison and R.B. Moore Soft Matter, 7, 6820-6827 (2011).

Session III: Scale-Bridging, Mesoscale Continuum Models and Applications

Ionic bilayers tail packing and mesoscale geometry

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ABSTRACT

Polyhedral shapes have been identified at the microscopic level in crystalline shells such as fullerenes, viral capsids and protein-based bacterial organelles. The most frequently found polyhedron in homogeneous crystalline shells is the icosahedron. We demonstrate that other geometries arise spontaneously in shells formed by more than one component. The spontaneous buckling of a crystalline shell with two coexisting elastic components at different relative concentrations is described. We provide computational and experimental evidence of the spontaneous buckling phenomena in shells made of mixtures of cationic and anionic amphiphiles, where electrostatics drives their co-assembly, and orders the assembly into faceted ionic structures with various crystalline domains. Our work explains the existence of various regular and irregular polyhedral shells found in nature, and provides the principles for designing nanocontainers with specific shapes and symmetries for numerous applications in material and life sciences.

Session III: Scale-Bridging, Mesoscale Continuum Models and Applications

Phase-field modeling of polycrystalline solidification: from needle crystals to spherulites

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ABSTRACT

Advances in the orientation-field-based phase-field (PF) models made in the past are reviewed. The models applied incorporate homogeneous and heterogeneous nucleation of growth centers and several mechanisms to form new grains at the perimeter of growing crystals, a phenomenon termed growth front nucleation. Examples for PF modeling of such complex polycrystalline structures are shown as impinging symmetric dendrites, polycrystalline growth forms (ranging from disordered dendrites to spherulitic patterns), and various eutectic structures, including spiraling two-phase dendrites. Simulations exploring possible control of solidification patterns in thin films via external fields, confined geometry, particle additives, scratching/piercing the films, etc. are also displayed. Advantages, problems, and possible solutions associated with quantitative PF simulations are discussed briefly.