

# Multiscale Modeling of Polymer Based Nanomaterials

J. S. Smith\*, D. Bedrov\*\*, O. Borodin\*\* and G.D. Smith\*\*

\*Wasatch Molecular Inc., 2141 St. Mary's Dr., ste 102, Salt Lake City, UT 84108, USA  
jssmith@xmission.com

\*\*Department of Materials Science and Engineering, University of Utah, 122 S. Central Campus Dr.,  
Room 304, Salt Lake City, Utah 84112, USA.

## ABSTRACT

In materials design and engineering there is a need for fundamental information that spans large scales of time and distances, from the quantum chemical nature of interactions to the macroscopic mechanical and electrical properties. In order to acquire technologically relevant information the most efficient modeling methodology for each time and length scale should be used. We have developed a new methodology using a synergy of ab initio quantum chemical (QC), atomistic molecular dynamics (MD), coarse grained molecular (CGM), and material point (MPM) computer simulation methods to explore materials behavior across these scales of interest. In this method it is important to represent the key physics (degrees of freedom) at each level explicitly while maintaining the influence of the other degrees of freedom implicitly through systematic parameterization or mapping. The mapping of important information between these different techniques is bidirectional and makes it possible to calculate the thermodynamic, dynamic, and electrical properties of materials with novel nanostructures. In order to illustrate these principles we will present a model of self assembling Poly(ethylene oxide) (PEO) decorated fullerenes in aqueous solutions which shows preferential formation of crystalline or linear aggregates depending on the density and orientation of the PEO tethers. Using this methodology we will also show how we can overcome the heterogeneous energy and time scales involved in modeling the micelle formation of triblock copolymers in aqueous solutions. Finally we will present our results showing calculations of viscoelastic properties of nanocomposites.

**Keywords:** multiscale modeling, molecular dynamics, polymers, micelles, fullerenes, nanocomposites

## 1 INTRODUCTION

Nano-structured polymer materials offer a number of attractive advances in material properties and are used in numerous applications. Addition of nano-sized filler particles to polymers to form reinforced nanocomposites and the formation of nano-sized micelles in solution and supermicellular structures are examples of diverse systems with important molecular processes which have a wide

range of length and time scales which cannot be addressed with a single simulation method. In order to bridge the length and timescales we have developed a multiscale modeling approach for simulations of polymer based nanomaterials.

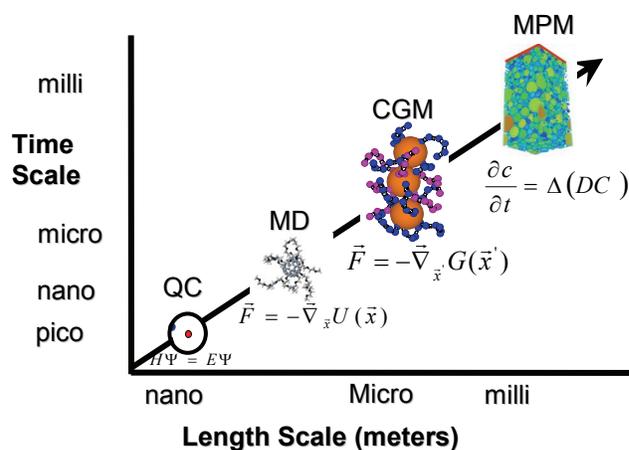


Figure 1: Illustration of the scales of modeling techniques in a multiscale approach.

The key to this methodology is the systematic elimination of the most computationally expensive degrees of freedom while retaining implicitly their influence on the remaining degrees of freedom in the coarse-grained model (CGM)[1]. The multiscale modeling strategy illustrated in figure 1 can be outlined as follows:

1. High level quantum chemistry calculations on model compounds and clusters are used to parameterize fully atomistic force fields for classical Molecular Dynamic (MD) simulations.
2. Fully atomistic MD simulations of low molecular weight polymers or small numbers of particles are conducted to provide molecular scale structural, conformational and dynamic properties and correlations to use in parameterizing CGMs.
3. CGMs which represent polymer and particle segments by single force centers are used to perform Langevine or Lattice Boltzman simulations to simulate realistically sized systems and access

longer timescales since these simulations are three orders of magnitude faster than atomistic MD simulations.

- At this point one of two directions can be taken, either the CGM model properties can be (a) upscaled or mapped to a continuum level model such as finite element or material point method (see section 4) or (b) equilibrated CGM structures can be reverse mapped to the atomistic MD model and simulations can be conducted to obtain atomic scale properties (see section 3).

In the remainder of this paper we will discuss this methodology as it relates to simulations of fullerenes in aqueous solution [2,3], PEO-PPO-PEO micelles [4] in solution, and nanocomposite materials [5].

## 2 PEO DECORATED FULLERENES

The aggregation of chemically realistic fullerenes ( $C_{60}$ ) and fullerenes with 6 PEO tethered chains evenly distributed on the surface in aqueous solution have been studied using a multiscale methodology [2,3]. It began with fully atomistic MD simulations of fullerenes using our validated quantum chemistry based force field to describe PEO – PEO and PEO – water interactions and a series of literature potentials and combining rules to describe all  $C_{60}$  interactions the details of which are discussed in reference 2. Consistent with previous studies a combination of umbrella sampling using a harmonic biasing potential between two fullerenes and the self consistent multiple histogram approach was used to determine the potential of mean force (PMF) between two bare and two tethered fullerenes in water solution (figure 2). Atomistic explicit solvent (AES) simulations of more than a few particles are prohibitively expensive due to the large number of solvent molecules (water) in the simulation. Therefore a coarse-grained implicit solvent model (CGIS) was parameterized.

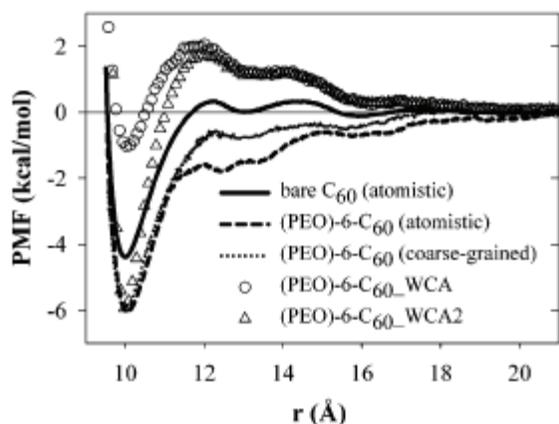


Figure 2: PMF between two bare and tethered fullerenes as a function of their center of mass separation,  $r$ , in aqueous solutions obtained from AES MD and CGIS model simulations at 298 K.

The CGIS model must reproduce the intramolecular and intermolecular structure of aqueous PEO solutions, the distribution of PEO segments around fullerenes, and the PMF between fullerenes. Each PEO chain is represented by a 6 bead chain with each bead corresponding to a  $CH_2-O-CH_2$  group. The interactions between these beads were adjusted to reproduce the intramolecular and intermolecular correlations from MD simulations of PEO chains in aqueous solutions. The fullerenes are represented by a single force center sphere with the  $C_{60} - C_{60}$  interaction set to the PMF of bare fullerenes in an aqueous solution. And finally the  $C_{60} - PEO$  interaction were parameterized to reproduce the PEO monomer distribution around the fullerenes from the MD simulations. The CGIS model of the tethered fullerenes reproduced well the PMF from explicit atomistic simulations as shown in figure 1.

Brownian MD simulations with this CGIS mode were used to compare the aggregation behavior of 1000 bare and 1000 decorated fullerene particles in aqueous solutions with fullerene volume fractions ranging from 0.07 to 0.25 at 298 K. As expected the bare fullerenes quickly aggregated into a single large cluster as illustrated in figure 3. However simulations of the PEO decorated fullerenes showed that they formed extended chainlike clusters that were dispersed in the system. The observed self assembly behavior of the PEO modified fullerenes is due to the preferential paths of approach between the particles due to the wrapping of PEO chains around the neighboring fullerene particle. The CGIS model used was able to exclude solvent degrees of freedom allowing the simulation of large sized systems which illustrated that chemical modifications of nanoparticles and nanoscale phenomenon can result in complex interactions that if understood can offer a variety of options for controlling the self-assembly of nanoparticles in solutions, polymer melts and blends.

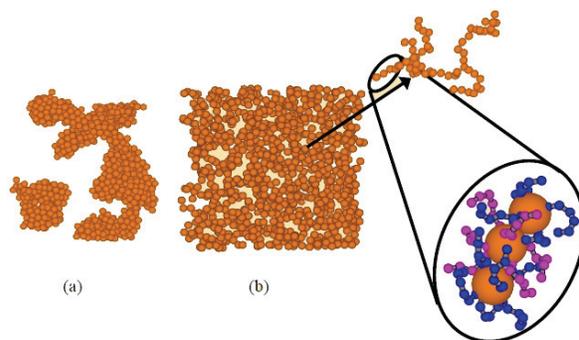


Figure 3: Illustration of (a) 1000 bare fullerenes aggregating in aqueous solution and (b) 1000 PEO modified fullerenes in chainlike clusters in solution at 298 K and concentrations of 0.07 volume fraction (PEO and water not shown). Also shown is an illustration of three aggregating CGIS model fullerenes with attached PEO chains.

### 3 TRIBLOCK COPOLYMER MISCELLES IN AQUEOUS SOLUTION

Poly(ethylene oxide) PEO based copolymers including triblock PEO – Poly(propylene oxide) – PEO and PEO – PPO –PPO triblock copolymers also known as pluronics are used in a variety of aqueous applications [1]. Experimental measurements show that the formation of a Pluronic micelle occurs in a complex multistage process. The fast process of molecules joining and leaving an incipient micelle occurs on the order of microseconds while the second process, a relaxation of micelle through merging and dissolution of micelles, is on the order of milliseconds. Because of the slow kinetics and large sizes of pluronic micelles it is impractical to use conventional MD or Monte-Carlo (MC) simulations to model these systems.

Explicit atom MD simulations of PEO/PPO melts and PEO/PPO/water solutions were conducted using quantum chemistry based force fields to obtain the intermolecular and intramolecular pair correlation functions between monomer centers of mass. A CGIS model was constructed by representing the PEO and PPO polymers as bead-spring polymers with each bead representing an ether oxide (EO) or propylene oxide (PO) monomer as a single force center located at the monomer center of mass. These bead-spring chains have harmonic bonds and bends and a specific 1 – 4 potential parameterized to correctly represent the intramolecular chain structure. The intermolecular CGIS model parameters were obtained using the inverted Boltzman potential to fit target functions based on the intermolecular radial distribution functions for the EO-EO, PO-PO, and EO-PO monomers from aqueous solutions (see Figure 4).

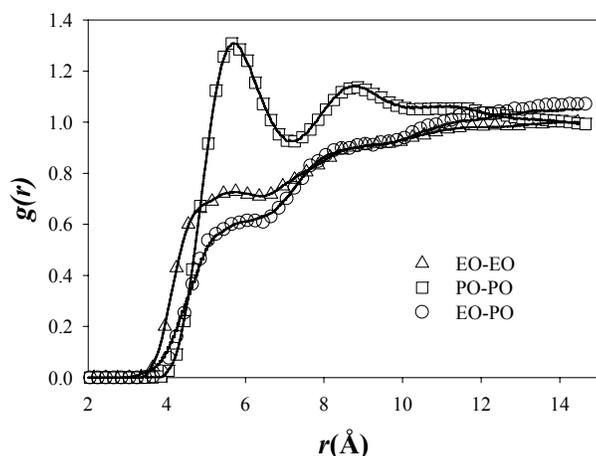


Figure 4: Intermolecular monomer-monomer pair distribution functions for ethers in aqueous solution at 298 K and 0.52 weight fraction of ethers as obtained from AES MD (symbols) and CGIS (lines) simulations.

CGIS simulations were set up with chain numbers estimated from experimental measurements (see figure 5). The micelles were generated then relaxed many times the time it takes for the micelle to completely decorrelate from its initial orientation. In this study the relaxed micelle configurations were mapped back to explicit atomistic MD simulations in order to study the distribution of water molecules, local chain conformations and other atomistic scale properties in the core and corona of the Pluronic micelle.

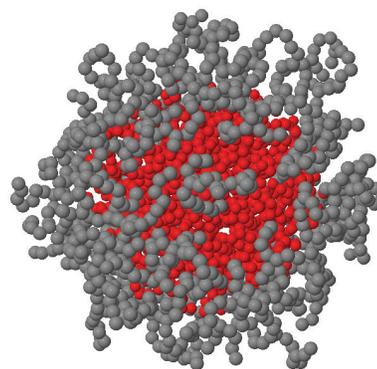


Figure 5: Representative illustration of a Pluronic micelle in the CGIS model.

The CGIS model is still unsuitable for accessing the second micellization process timescale (milliseconds). Therefore, the multiscale modeling protocol described above has to be further enhanced to effectively access larger length and longer time scales and to allow the prediction of the equilibrium distribution of micelle sizes as a function of Pluronic concentration and temperature. One of the approaches which we are currently investigating is the Parallel Tempering method, modification of which we have recently developed and successfully applied for equilibration of model self-assembling polymer networks [5].

### 4 VISCOELASTIC PROPERTIES OF POLYMER NANOCOMPOSITES

The properties of polymers filled with nanosized particles can be controlled through modification of the interfacial polymer properties due to the large specific interfacial areas between the nanoparticles and polymer matrix. A general approach to the multiscale modeling of polymer nanocomposites has been developed [4]. The methodology consisted of three steps: (1) using explicit atom MD simulations to generate viscoelastic properties of both the bulk polymer and the interfacial polymer as a function of the distance between the polymer and the solid surface, (2) using the bulk and interfacial polymer properties to perform stress-relaxation simulations using the material-point-method to extract the overall nanocomposite properties.

MD simulations were conducted using idealized bead-necklace polymer chains surrounding an embedded periodic cylinder as shown in figure 6. The strength of the cylinder surface to polymer interactions were varied and it was found that the stronger the change in the interfacial polymer viscoelastic properties the stronger is the need of a position dependent description of those properties in the simulations. The polymer density oscillations near the cylinder surface are used to define interfacial layers, and the properties of these layers (shear modulus  $G(t)$ ) are highly perturbed near the surface and become more bulk like farther from the surface (after 4 layers). The key assumption is that the shear modulus of the layers can be calculated from mean squared displacement data of the beads from the MD simulations.

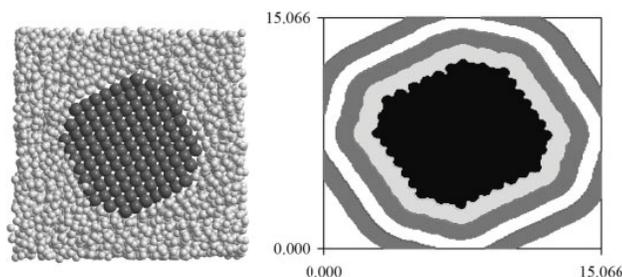


Figure 6: Illustration of MD simulations (left panel) and MPM simulations (right panel) of a cylinder embedded in a bead-necklace polymer matrix with 30 vol% filler.

This data was used to parameterize a MPM model and conduct stress-relaxation computational experiments on the composites to obtain average composite mechanical properties. For comparison the shear modulus of these composites were calculated directly from MD simulations. For all MPM simulations, ignoring the position dependence of the shear modulus in the polymer around the nanocomposites under predicted the composite shear modulus when compared to the modulus calculated from MD simulations. Excellent agreement between MPM and MD predictions was achieved when interfacial polymer (position dependent) properties were included in the MPM calculations. This illustrated that the information obtained from a CGM can be mapped to a continuum level model such as MPM in order to obtain average nanocomposite properties.

## 5 CONCLUSIONS

The use of multiscale methodologies that span the simulation length and time scales on a variety of systems has been reported. By using the appropriate method for the scale of interest and mapping from one level to the other by eliminating certain degrees of freedom but retaining their influence implicitly on the physics of the problem these length and time scales can be effectively bridged. While in

the coarse-grained simulations presented we were able to exclude certain degrees of freedom such as the solvent molecules, caution must be exercised in excluding degrees of freedom that have nontrivial and non-isotropic contributions to the system (i.e. the PEO chains tethered to the fullerenes).

## REFERENCES

- [1] D. Bedrov, C. Ayyagari and G. D. Smith, submitted to *Journal of Chemical Theory and Computation*, 2006.
- [2] D. Bedrov, G. D. Smith, and L. Li, *Langmuir*, 21, 5251 – 5255, 2005.
- [3] L. Li, D. Bedrov and G. D. Smith, *Journal of Chemical Physics*, 123, 204504, 2005.
- [4] O. Borodin, D. Bedrov, G. D. Smith, J. Nairn and S. Bardenhagen, *Journal of Polymer Science: Part B: Polymer Physics*, 43, 1005 – 1013, 2005.
- [5] C. Ayyagari, D. Bedrov and G. D. Smith, *Journal of Chemical Physics*, 123, 124912, 2005.