

# Nanoengineered Materials: From Polymer Composites to Structured Adsorbents

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The challenge for nanoscale modeling and simulation is to bridge the length and time scales that are necessary to connect nanostructure of the material with its macroscopic properties. This challenge can only be met by combining the efforts of individual researchers who collectively are expert in a wide range of computational and theoretical techniques. The team we have assembled from the University of Pittsburgh (including senior collaborators, R. D. Coalson and K. D. Jordan, Department of Chemistry) and M.I.T. contains representation and perspectives from the traditional disciplines of physics, chemistry, chemical engineering and materials science. Our aim is to attack problems of critical importance to the energy and chemical industries, for example, the efficient design of nanocomposites, polymeric batteries, adsorbents for hydrogen storage and molecular sieves for gas separation.

For optimization of the design of nanocomposites which, for the most part in our research, will comprise mixtures of polymer blends and nanoscale solid particles, one will have to employ a raft of computational techniques, ranging continuously from quantum mechanical calculations through coarse-grained modeling and finally to macroscopic treatments, for example. Using this range of techniques our group aims ultimately to connect nanoscale characteristics of the filler particles to the mesoscale morphology of the mixture during and at the conclusion of processing, and finally to the macroscopic mechanical, electrical and optical properties of the composite. Polymer nanocomposites of particular interest in the development of polymeric batteries will be included as part of this research. Finally, the special nature and importance of carbon nanotubes that make them candidates for components of gas storage devices, separation devices and sensors dictates that such materials as additives are included in the program. In the following, preliminary results of the mesoscale modeling and simulation subgroup comprising Balazs, Jasnow and collaborator R. D. Coalson is reviewed first on filled diblock copolymer blends and on polymer translocation through membranes. This will be followed by the molecular level work of Johnson and collaborator K. D. Jordan, and finally by the meso to macroscopic level computations of Carter. Finally, an example of calculations on Li loading by Ceder is shown.

Mixtures of solid nanoparticles and A-B block copolymers can yield complex highly ordered composites for a variety of applications. The specific morphology and utility of these materials depends on a variety of nonuniversal properties of the mixture such as the size and volume fraction of the particles, as well as the copolymer architecture. We report here our initial efforts at developing models for calculating the morphology and thermodynamic properties of such mixtures, schematically indicated below.

The first method we report here combines a self-consistent field theory (SCFT) for the polymer and a density functional theory (DFT) for the nanoscale particles. The SCFT appears to be the method of choice for describing thermodynamic behavior of pure polymeric systems while DFT is known to capture ordering and phase behavior in colloidal systems. The combined techniques have been applied to diblock/particle mixtures and reveal new self-assemblies in which both particles and polymers organize into mesoscopically regular patterns. In particular, we have begun to delineate conditions in which the polymer nanostructure can drive the filler particles to

self-assemble into nearly continuous “nanowires.” The method can be straightforwardly generalized to composites involving other copolymer architectures (triblocks, combs, stars) or other kinds of blends.

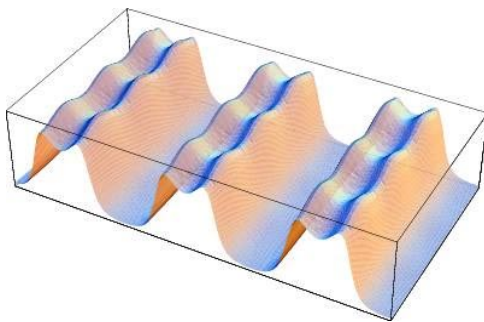


BCP + Particle

The SCFT locates functional extrema, so it is necessary to supplement these calculations with kinetics of the evolution of the structures. Balazs and coworkers have carried out preliminary simulations for the kinetics treating the copolymer at the coarse grained level and the particles as discrete, in 3D. Preferential interaction of the particles with one species of the diblock leads to interesting self-organized structures.

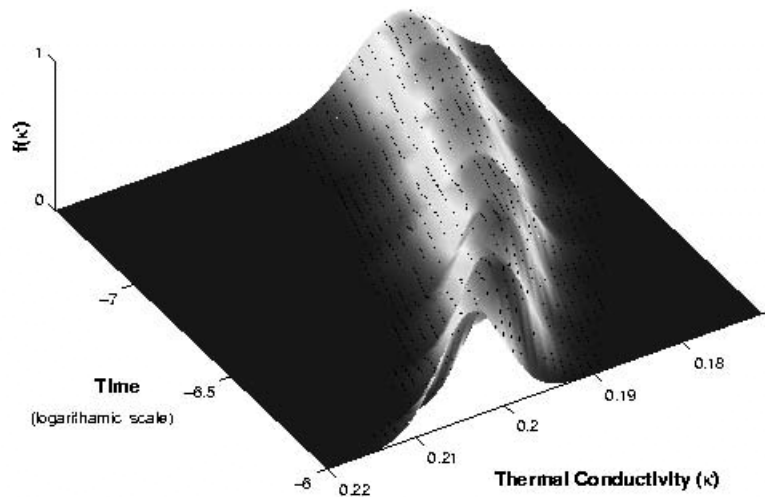
The essential densities we need for this description include the local polymeric concentrations, the local particle concentration and the probability distribution of particle centers. The particles are assumed to have a preferential attraction to the A block material which conditioned can be realized for example by coating the particles. The free energy contains the usual Flory-Huggins (enthalpic) term for the diblock with the addition of an interaction term between particles and the diblock. An additional term includes the contribution for a single diblock chain in the self-consistent field, and finally there is a contribution for the particles. The last contribution contains a phenomenological term taken from the description of hard spheres (Tarazona weighted density functional approach using the Carnahan-Starling excess free energy for a hard-sphere fluid). Incompressibility is assumed. Our method of solution is an iterative technique based on the scheme of Drolet and Fredrickson.

In the figure below a two-dimensional SCF solution for the local A volume fraction is shown in a particular parameter range allowing for the formation of lamellae with organized nanowires formed of the filler particles in the center of the A microdomains. The dimpled region represents excluded A material and (not shown) a high density of filler particles. This self-organized structure has a great deal of potential for a variety of technological applications. This type of morphology is expected and observed when the particle volume fraction takes on intermediate values, that is, values neither too large nor too small. We will continue investigations of this interesting self-assembled structure.



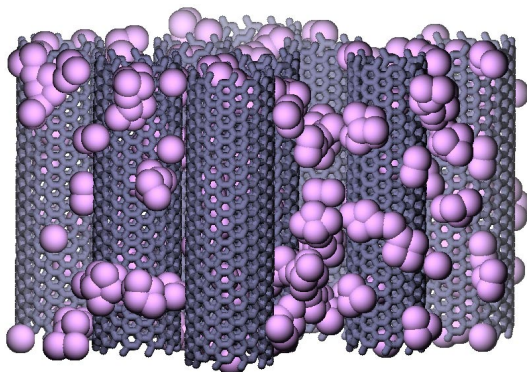
The results of the coarse-grained and other mesoscale simulations yielding relevant structures will be fed into the computational techniques at the macro level. As an example Carter and coworkers have considered the probability distribution (over an ensemble of initial conditions) of a macroscopic response (e.g., thermal conductivity) of a phase separating binary in which the coexisting phases have differing thermal properties. In the figure below a

preliminary calculation of the resulting macro property (thermal conductivity) as a function of time as the system undergoes phase separation, described at the TDGL level. This work represents an important part of the mesostructure – macroproperty link in the research program.



An additional line of work within the coarse grained level involves polymer translocation dynamics. The simulations utilize dynamical monte carlo and describe translocation through a pore. Previous applications have been in a biological context, and future applications of the group are expected to involve organic/inorganic interfaces and transport in porous media, the latter relevant to the development of materials for battery design.

Preliminary results for some microscopic level computations involve the clustering of atoms (e.g., Li) on single walled nanotubes (J. K. Johnson and collaborator K. D. Jordan). Ultimately full QM calculations, including electron correlation, of the charge transfer and response of nanotube bundles with adsorbents will be relevant to conductor and battery design.



Rapid in and out diffusion of lithium in small oxide or metal particles is the key element for rechargeable lithium batteries with high power density. The concentration gradients, associated with the large Li fluxes can cause stresses that are well above the fracture stress of the material. As a result the electrode particles break up into smaller parts upon repeated cycling of Li. Using a combination of density functional theory, kinetic Monte Carlo and continuum simulations, Ceder and coworkers have modeled this process. The figures below show the calculated Li composition

profile during Li removal, and its corresponding stress state.

