

Dispersions of Nanoparticles in Polymers: Interfacial and Bulk Behavior

Amalie L. Frischknecht¹, Erin S. McGarrity², and Michael E. Mackay³

¹Sandia National Laboratories, Albuquerque, NM

²Michigan State University, East Lansing, MI

³University of Delaware, Newark, DE

Scientific Thrust Area: Theory and Modeling of Nanoscale Phenomena

Proposal Title: Effects of Nanoparticles on Polymer Film Dewetting

Research Achievement

Polymer nanocomposites display a variety of unique features when the nanoparticle radius is smaller than the radius of gyration of the polymer, including miscibility of the nanoparticles in the polymer and assembly of the nanoparticles at surfaces. Thin films of these blends have many possible applications such as chemical sensors, computer memory, supercapacitors and flexible organic solar cells. The realization of these technologies depends on understanding and controlling the interactions in the system to obtain self-assembled, functional nanostructures. Of particular interest to us is the interplay of entropic effects and van der Waals interactions, which are key in thin film stabilization and placement of the nanoparticles at particular interfaces. We are using various theoretical techniques to elucidate the mechanisms involved in these nanoparticle/polymer composites.

Polymer/Nanoparticle Blends at a Substrate

In thin films of polystyrene (PS) nanoparticles blended with PS homopolymer, we have shown that the nanoparticles form a monolayer on the substrate. Since the polymer and nanoparticles are chemically compatible, the forces driving the nanoparticles to the substrate are thought to be entropic in origin [1]. The presence of about a monolayer of nanoparticles at the substrate has the additional surprising property of preventing the dewetting of the films.

We modeled this system as a mixture of hard spheres and freely jointed hard chains, near a hard wall. Using a fluids density functional theory (DFT), we showed that there is a first order phase transition (see Fig. 1) in these blends in which the nanoparticles expel the polymer from the substrate to form a monolayer at a certain nanoparticle concentration. The nanoparticle transition concentration depends on the length of the polymer and on the nanoparticle diameter. The phase transition is due to both packing entropy effects related to size asymmetry between the components, and to the polymer configurational entropy, justifying the so-called “entropic push” observed in experiments. The magnitude of the free energy gain upon addition of nanoparticles is consistent with experiment.

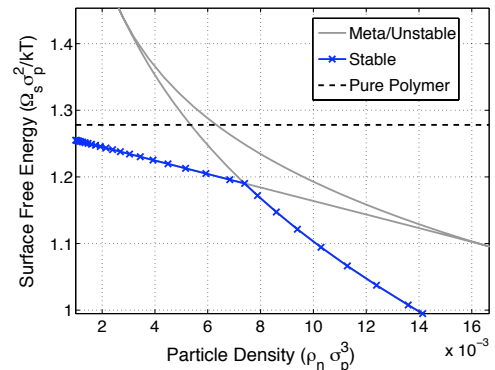


Fig. 1: Free energy curve showing a change in slope at the phase transition.

Bulk Mixtures

Neutron scattering experiments by the Mackay group showed that for PS nanoparticles blended in PS, the polymers undergo a significant amount of chain expansion as the nanoparticle volume fraction increases [2]. This is surprising in that chain expansion costs free energy, which should therefore make the nanoparticles less miscible in the polymer, but the nanoparticles were indeed miscible. There is considerable controversy in the literature over whether the addition of nanoparticles to a polymer melt causes chain expansion. To address this question, we performed self-consistent polymer reference site model (SC/PRISM) theory calculations. PRISM is a liquid state theory that predicts the equilibrium structure of polymeric fluids. In self-consistent PRISM theory, the intramolecular structure of the polymer chains is calculated by performing a single-chain Monte Carlo simulation, in a solvation potential provided by PRISM theory that represents all the intermolecular interactions in the system. This allows a determination of the radius of gyration R_g from the single chain simulation, without the computational cost of performing a many body simulation in a dense fluid.

In the first SC/PRISM calculations on nanoparticle/polymer blends, we find that the nanoparticles do indeed perturb the polymer chain dimensions. Fig. 2 shows the value of R_g , relative to the value for the pure polymer melt R_{g0} , as a function of nanoparticle volume fraction ϕ_n . The polymers expand with increasing nanoparticle volume fraction, in semi-quantitative agreement with our experimental results.

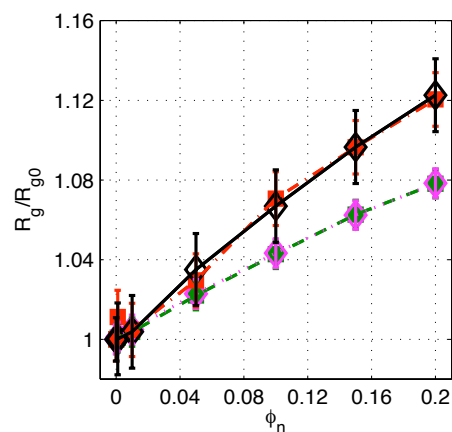


Fig. 2: Chain expansion for nanoparticles of diameters 5 (squares) and 6.2 (diamonds) for chains of length 40 (lower curves) and 80 (upper curves).

Future Work

We plan to explore the effects of attractive interactions on the phase transition described above for nanoparticle/polymer blends near a substrate. We will also extend the fluids-DFT to include liquid/vapor interfaces in order to model truly thin films. These results will be compared with experimental results on other nanoparticles, such as CdSe quantum dots, mixed in polymers.

References

- [1] R. S. Krishnan et al., *J. Phys. Condens. Matter* 19, 356003 (2007).
- [2] A. Tuteja, P.M. Duxbury, and M.E. Mackay, *Phys. Rev. Lett.* 100, 077801 (2008).

Publications

1. E.S. McGarrity, A.L. Frischknecht, L.J.D. Frink, and M.E. Mackay, "Surface-induced first-order transition in athermal polymer-nanoparticle blends," *Phys. Rev. Lett.* 99, 238302 (2007).
2. E. S. McGarrity, A. L. Frischknecht, and M. E. Mackay, "Phase behavior of polymer nanoparticle blends near a substrate", *J. Chem. Phys.* 128, 154904 (2008).
3. E. S. McGarrity, P. M. Duxbury, M. E. Mackay, and A. L. Frischknecht, "Calculation of entropic terms governing nanoparticle self-assembly in polymer films," *Macromolecules* 41, 5952 (2008).
4. A. L. Frischknecht, E. S. McGarrity, and M. E. Mackay, "Expanded chain dimension in polymer melts with nanoparticle fillers," submitted to *Phys. Rev. Lett.* (2009).