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Notes

Calculation of Entropic Terms Governing Nanoparticle Self-Assembly in Polymer Films

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Directed self-assembly of nanoparticle arrays and bulk heterostructures in thin polymer films underlie a variety of emerging technologies, including high-density information storage,[1] chemical sensors,[2] crack detection and self-healing in materials,[3,4] and flexible solar cells.[5] Key to the functionality of these applications is the self-assembly of the nanoparticles at the interfaces inside the films.[4,6,7] This assembly is driven by a subtle interplay of enthalpic and entropic forces between the constituents of the blend.[7–9] In most of the applications cited above, the enthalpic contributions are dominated by dispersion terms,[10] for which sophisticated theories are available.[11,12] In this communication, we use a fluids density functional procedure to calculate the entropic contribution to nanoparticle self-assembly in athermal polymer/nanoparticle composites and compare these calculations to simple scaling estimates.

In a polymer/nanoparticle mixture, self-assembly of nanoparticles at a hard substrate is entropically favored since it releases polymer chains from the constraints imposed by the substrate.[8] In previous experiments with polystyrene (PS) films blended with polystyrene nanoparticles, which are dominated by entropic forces, it was shown that the nanoparticles assemble at the substrate upon annealing.[7] An estimate of the magnitude of these forces can be determined by calculating the change in free energy using a simple balance of three terms.[6,7] The first two terms, which are related to the nanoparticle translational entropy and the entropy and enthalpy of mixing, are discussed elsewhere.[7] The final term is due to the displacement of the polymer by the nanoparticles at the substrate and is the focus of this work. In the PS/PS blends mentioned above, the nanoparticles segregate to the substrate and exclude the polymer as the mixing entropy is overcome by the chain configurational entropy. When this occurs, the system gains (relative to the mixed system) $\alpha k_B T(\sigma_n/\sigma_p)^3$ of entropy, where σ_n is the nanoparticle diameter, σ_p is the statistical segment size, $k_B T$ is the Boltzmann constant times the temperature, and α is the number of degrees of freedom gained by a polymer segment by moving away from the wall. In terms of surface free energy per unit area F_{ch} we have

$$\Delta F_{ch} = \alpha k_B T \frac{V_n}{V_s {\sigma_n}^2} \tag{1}$$

where V_n and V_s are the volumes of the nanoparticle and statistical segment, respectively. On the basis of the experimental data, we have suggested that α has lower and upper bounds of 0.01 and 1.0, respectively.[7]

In order to test the simple estimate (1) and to determine a more precise value of α for a well-characterized model system, we have performed fluids density functional theory (DFT) calculations on athermal polymer/nanoparticle blends. In previous work, Lee et al. found that nanoparticles segregate from a diblock copolymer melt to form a layer on the subsrate, using a combined self-consistent field/DFT method.[9] In our past work on athermal nanoparticle/homopolymer blends, we showed that nanoparticle segregation from a homopolymer melt is a first-order phase transition where the nanoparticles form a monolayer on the substrate at a certain nanoparticle density ρ_n^*.[13] This phase transition was shown to be dependent on chain length. It was found that the chains had to be at least several monomers long in order to have a transition at all. (There is no such transition in binary sphere blends.) The surface free energy at the transition for these systems becomes chain length independent when the chains are long enough (less than 0.2% difference between 80-mers and 100-mers). We also showed that the nanoparticle diameter is a crucial parameter, and the phase transition only takes place in a certain range of diameters (1.75−2.25 statistical segment units).[14] Below, we extended these latter calculations to compare the free energy gain from this layering transition in our system to the simple form in eq 1.

Fluids DFT is based on the calculation of spatially varying density distributions $\rho_\gamma(\mathbf{r})$ for species γ, which minimize a functional $\Omega[\rho_\gamma]$ for all points $\mathbf{r}$ in the domain.[15] This minimum is found using the variational calculus in an open (chemical potential (μ), volume (V), temperature (T)) ensemble, i.e., $(\delta\Omega[\rho_\gamma]/\delta\rho_\gamma)_{\mu,V,T} = 0$, and corresponds to the grand potential for the system. The functional that we use is

$$\Omega[\rho_\gamma] = F_{id}[\rho_\gamma] + F_{ex}[\rho_\gamma] + \sum_\gamma \int d\mathbf{r}\, \rho_\gamma(\mathbf{r})[\phi_\gamma(\mathbf{r}) - \mu_\gamma] \tag{2}$$

where $F_{id}[\rho_\gamma]$ and $F_{ex}[\rho_\gamma]$ are the ideal gas and excess Helmholtz free energies, $\phi_\gamma(\mathbf{r})$ is an external potential on each species due to the substrate, and μ_γ is the chemical potential of each species. We used the White Bear functional[16] for the hard-sphere contribution and the Tripathi/Chapman[17] functional for the chain contribution to $F_{ex}[\rho_\gamma]$. This functional assumes that the chain monomers represent isotropic Kuhn monomers. The effects of monomer anisotropy should not be discernible in such a coarse-grained system.

The model system consisted of a blend of hard-sphere nanoparticles with diameter σ_n and freely jointed 100-mer hard-sphere chains with segment diameter σ_p. This length was chosen because it is beyond the threshold for polymer-like behavior.

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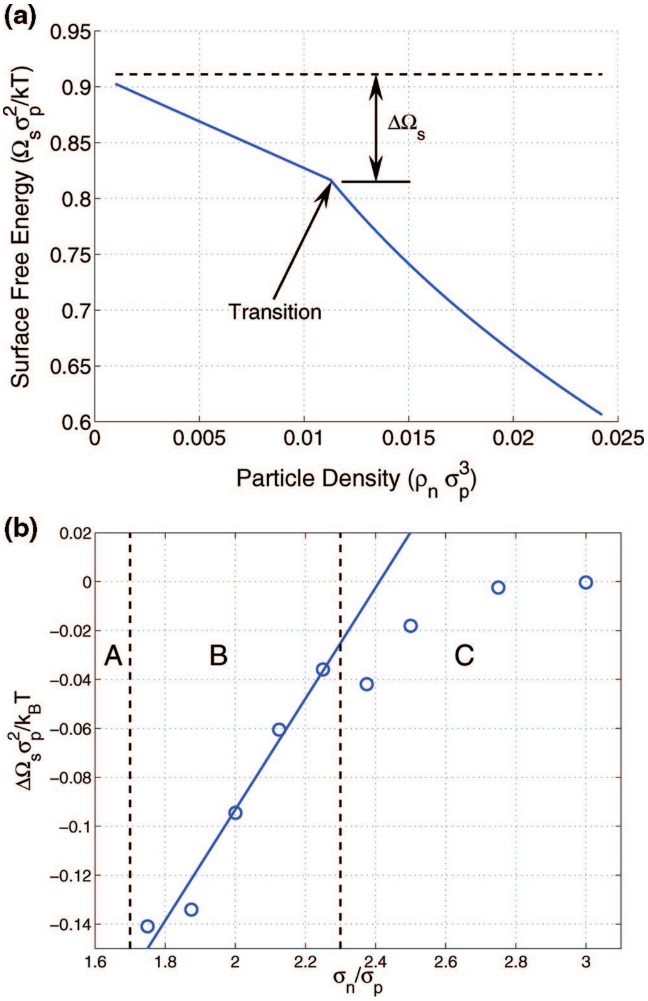

Figure 1. (a) Surface free energy vs nanoparticle density for $\sigma_n = 2\sigma_p$, $N = 100$, and $\eta = 0.3665$. The abrupt change in slope of this curve at $\rho_n^* = 0.011\,27$ ($\eta_n^* = \pi\rho_n^*\sigma_n^3/6 = 0.047\,20$) is indicative of a first-order layering transition. The dashed line is the free energy of a neat polymer system with $N = 100$ and $\eta = 0.3665$. (b) Surface energy difference, $\Delta\Omega_s$, between a ($N = 100$) neat polymer and blends containing nanoparticles (at $\eta = 0.3665$) as a function of nanoparticle diameter σ_n. The circles represent the difference as calculated from DFT at a monolayer surface coverage of the substrate.

The blend was modeled at a concentrated solution-like density with a total packing fraction $\eta = \pi(\rho_n\sigma_n^3 + \rho_p\sigma_p^3)/6 = 0.3665$. The computational domain for these calculations was a large, one-dimensional box ($L = 40\sigma_p$) with a hard wall and reflective boundary conditions, making the external potential for the system $\phi_\gamma(z) = \infty$ for $z \leq \sigma_\gamma$ and $\phi_\gamma(z) = 0$ otherwise.

In the fluids DFT we calculate the excess surface free energy $\Omega_s \equiv \Omega - \Omega_{bulk}$, where the first term is the free energy in the presence of a hard wall and the second term Ω_{bulk} is the free energy in the absence of a hard wall. The fluids DFT includes all the entropic contributions to the free energy, i.e., translational, packing, and chain configurational entropy, whereas eq 1 is an estimate of just the gain in configurational entropy if the polymer moves away from the substrate and is replaced by nanoparticles. This term can be approximately extracted from the fluids DFT as follows. In a neat polymer film with no nanoparticles, the only contributions to the free energy are the chain configurational entropy and the monomer packing entropy. As nanoparticles are added, the free energy decreases as shown in Figure 1a due to the favorable mixing entropy. At the phase transition (ρ_n^*), the free energy for the mixed state is the same as the free energy for the segregated state, so at this point the gain in configurational entropy balances much of the mixing entropy when the polymer moves away from the substrate. In the segregated state, the nanoparticles have lost much of their translational entropy, so this contribution to Ω_s is small. Furthermore, in the mixed state at the phase transition, the polymer density profile is nearly the same as in the neat polymer film, so the packing entropy contribution to Ω_s is about the same in the two states. Then, the difference in free energy between the neat polymer and the blend in the segregated state at the phase transition will be dominated by the chain configurational entropy. We therefore take $\Delta\Omega_s = \Omega_s(\rho^*) - \Omega_s(0)$ as the DFT prediction for the quantity in eq 1. In particular, we expect that any extra entropic contributions to $\Delta\Omega_s$ (such as translational entropy of the nanoparticles remaining in the bulk) will not depend strongly on nanoparticle diameter. Note that $V_n/(V_s\sigma_n^2) = \sigma_n^3/(\sigma_p^3\sigma_n^2)$, which allows us to rewrite eq 1 as

$$\frac{\Delta F_{ch}\sigma_p^2}{k_BT} \approx \frac{\Delta\Omega_s\sigma_p^2}{k_BT} = \alpha\frac{\sigma_n}{\sigma_p} \qquad (3)$$

which is linear in the ratio σ_n/σ_p, when σ_p is constant. Thus, the functional dependence of $\Delta\Omega_s$ as calculated from the DFT should be compared to eq 3.

The surface free energy gain $\Delta\Omega_s$ is plotted as a function of the normalized nanoparticle diameter in Figure 1b (open circles). This plot shows the DFT estimate of the entropic "push" driving nanoparticles to the substrate.[4,6,7] Figure 1b is divided into three regions by dashed vertical lines which correspond to different blend behaviors. In region A ($\sigma_n < 1.75\sigma_p$) there is no layering transition—the nanoparticles replace the polymer smoothly and in direct proportion to their concentration. In region B ($1.75\sigma_p \leq \sigma_n \leq 2.25\sigma_p$) the system undergoes a layering transition in which a dense nanoparticle layer forms at the substrate. This layer has an areal density at or above random close packing (0.82). For sufficiently large nanoparticles ($\sigma_n > 2.25\sigma_p$) the morphology changes (discontinuously) to one in which the nanoparticle layer is loosely packed and no longer adjacent to the substrate.[14] There is no longer an entropic gain for the polymer, and thus the free energy gain $\Delta\Omega_s$ goes asymptotically to zero. This state has not been observed in experiment and can be attributed to a variety of issues, including the absence of dispersion forces in the DFT calculations, the fact that the DFT used considers variations in density only in the direction normal to the substrate, the substrate in the DFT calculation is perfectly flat, and the fact that the nanoparticle used in the theory is hard whereas in many of the experiments soft polymer nanoparticles are used.

Nevertheless, the points in regime B, where the entropic segregation to the substrate occurs, can be compared to the simple prediction of eq 1. In region B of Figure 1b, and for fixed σ_p, the DFT data are indeed linear in σ_n/σ_p as predicted by the simple theory. Moreover, from the solid line in this figure we extract $\alpha = 0.21 \pm 0.01$, which is in good agreement with our previous estimates based on the experimental data.[7]

In the relevant regime, the DFT calculations thus support the simple scaling prediction of eq 1. This is very encouraging and reveals several interesting issues which need further investigation, including the reason why DFT undergoes a transition to a different state in regime C of Figure 1b, the related question of whether soft nanoparticles, as used in many experiments, have the same qualitative behavior, and the effect of segment shape and stiffness on the entropic gain.

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