

## Do “Nonequilibrium” Effects Control Strong Surface Segregation from Polymer Blends?

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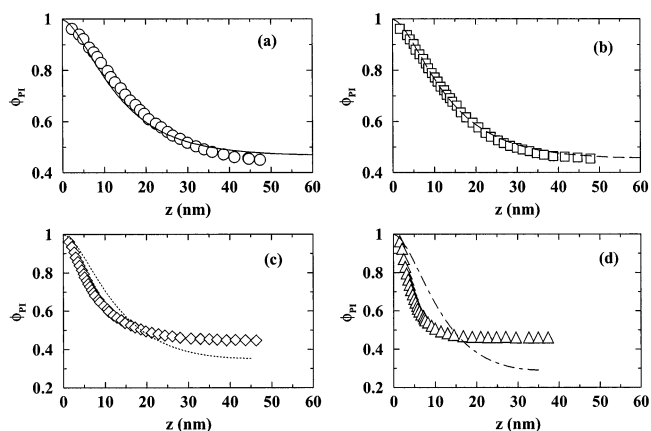
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**I. Introduction.** Experiments and theories on weakly segregating polymer blends show that the surface segregation decreases with decreasing film thickness.<sup>1</sup> This result has been attributed to the fact that, if the segregation were unaffected by thickness, the gradients would increase with decreasing thickness due to the overlap of profiles from the two surfaces. Since an increase in gradients is unfavorable to the free energy of the system, the blend responds by decreasing gradients and hence the concentration profiles “flatten” with decreasing thickness. In contrast to these ideas, recent measurements on an elastomer blend, deuterated poly-(butadiene)/ poly(1,4-isoprene) [dPB/PI] close to its critical point, where one of the components is strongly adsorbed to the surface, demonstrate a thickness independence to the surface composition.<sup>2,3</sup> Further, the composition profiles become sharper with decreasing film thickness, a qualitatively different behavior from that demonstrated by weakly segregating blends.<sup>1</sup>

To understand the origins of these results, we begin by using the Landau–Ginzburg mean field form proposed by Flebbe et al.<sup>4</sup> We use a strong surface affinity for PI to create a constant surface composition as in the experiments with varying thickness. However, we find that the theory cannot capture the spatial dependence of the experimentally determined concentration profiles, especially for film thicknesses smaller than 100 nm (see Figure 1). We then provide two means of rationalizing this result and conclude that it is probably caused by a layer of immobilized chains which are irreversibly pinned to the surfaces in the time scale of the experiments.

**II. Theoretical Development. Landau–Ginzburg Theory.** We consider a model miscible system between two identical parallel impenetrable surfaces separated by a distance  $D$ . We assume that the system is homogeneous in the plane parallel to the surfaces, and hence, we only consider variations in the perpendicular direction. This assumption is reasonable since it is supported by recent studies on the surface composition of dPS/PVME films using scanning SIMS in the single phase.<sup>5</sup> Also, experimentally it has been observed that PI segregates symmetrically to both the Si and air surfaces.<sup>3</sup> Due to the inherent symmetry of the system, we denote the center of the film by  $z = 0$  and thus limit our solution to one of the half-spaces. The system free energy,  $\Delta F$ , is written as<sup>4,6</sup>



**Figure 1.** Volume fraction of polyisoprene ( $\phi_{PI}$ ) as a function of the distance from the air surface ( $z$ ). Plots a–d correspond to film thicknesses of 170, 140, 90, and 70 nm respectively. The open symbols represent the experimental data taken from the paper by Grull et al. The lines represent the fits of the profiles to the mean field theory with  $\mu_1 = 0.5$ .

$$\frac{\Delta F}{k_B T} = \frac{2}{a^3} \int_0^{D/2} dz \left\{ f[\phi(z)] + \kappa(\phi) \left[ \frac{d\phi(z)}{dz} \right]^2 \right\} + \Phi_S \quad (1)$$

where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature, and  $\Phi_S$  is the bare surface free energy. In the case of a short-range surface field, a common form for the bare surface free energy is<sup>6</sup>

$$\Phi_S = -\mu_1 \phi_s - \frac{1}{2} g \phi_s^2 \quad (2)$$

where  $\phi_s$  is the surface composition,  $\mu_1$  is the strength of the surface potential, and  $g$  accounts for the “missing neighbor” effect near the surface. It is also possible to model the effect of surfaces as long-ranged with the following form,

$$\begin{aligned} \Phi_S(z) \equiv -\phi(z)\mu_S(z) &= -\mu_1 \phi(z) \left[ \frac{1}{(D/2 - z)^n} + \frac{1}{(D/2 + z)^n} \right], \quad |z| < D/2 \\ &= -\phi_s \mu_1, \quad z = \pm D/2 \end{aligned} \quad (3)$$

where  $n = 3$  corresponds to the long-ranged van der Waals surface forces. Note that we have assumed the “missing neighbor” effect  $g(\infty\chi) = 0$  for convenience. Previous work<sup>7</sup> has shown that the form of the surface potential does not cause any qualitative changes to the surface segregation results over the parameter range relevant to this work, and we treat the surface forces to be long-ranged with just one parameter,  $\mu_1$ , that determines the strength of the surface potential. Also, since we are not concerned about the composition profiles as a function of temperature,<sup>8</sup> we shall keep the value of  $\mu_1$  constant in the model. The integral in eq 1 has two terms, the free energy of mixing in a homogeneous system ( $f[\phi(z)]$ ) and the energy penalty associated with the formation of a composition gradient.  $f(\phi)$  is represented by the incompressible Flory–Huggins form<sup>9</sup>

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$$f(\phi) = \frac{\phi}{N_A} \log \phi + \frac{1-\phi}{N_B} \log(1-\phi) + \chi\phi(1-\phi) \quad (4)$$

where  $N_i$  is the degree of polymerization of component  $i$  and  $\chi$  is the interchange energy parameter. In the weak segregation limit<sup>6,10</sup>  $\kappa(\phi) = a^2/[36\phi(1-\phi)]$ , where  $a$  is the Kuhn length of the chains. While this form is strictly valid only if the correlation length of composition fluctuations,  $\xi \gg R_g$ , the experimental data of Grull et al.<sup>3</sup> reveal that this condition is violated for all film thicknesses. A more appropriate form is the strong segregation result<sup>11</sup>  $\kappa(\phi) \equiv a^2/[18\phi(1-\phi)]$ . Since the two forms were found to only result in minor quantitative differences in the final surface segregation results, we will limit our attention to the strong segregation form. The total free energy  $\Delta F$  in eq 1 must be minimized with the constraint of mass conservation to obtain the equilibrium composition profile. This problem can be reduced to solving the following Euler–Lagrange equation

$$\frac{\delta(\Delta F)}{\delta\phi} = \frac{\partial f(\phi)}{\partial\phi} - \frac{\partial\kappa(\phi)}{\partial\phi} \left(\frac{d\phi}{dz}\right)^2 - 2\kappa(\phi) \frac{d^2\phi}{dz^2} - \mu_S(z) = C_m \quad (5)$$

with the following boundary conditions,

$$\begin{aligned} 2\kappa(\phi) \frac{d\phi}{dz} \Big|_{z=D/2} &= -\mu_1 \\ d\phi/dz \Big|_{z=0} &= 0 \end{aligned} \quad (6)$$

The second boundary condition arises out of the symmetry in the composition profile about  $z = 0$ .  $C_m$  in eq 5 is a constant which can be shown to be equal to the exchange chemical potential in a semi-infinite system. For systems with finite film thicknesses, the magnitude of  $C_m$  is a measure of the deviation of the film thermodynamics from that of the coexisting bulk.

**Model Parameters.** The parameters of the theory were chosen to be consistent with the experiments on dPB/PI, i.e.,  $N_{\text{dPB}} = 1733$  and  $N_{\text{PI}} = 2088$ . Using a Kuhn size of  $a = 0.7$  nm and assuming Gaussian conformations yield the radii of gyration of dPB and PI to be  $\sim 12$  and  $\sim 13$  nm, respectively. A temperature of 298 K was incorporated using the previously reported empirical relationship relating  $\chi$  to temperature:  $\chi = 0.00541 - 1.4234/T$ .<sup>3</sup> Since the reported lower critical solution temperature for the blend is  $\sim 328$  K, we are operating in the single phase regime where  $(T_c - T)/T_c \sim 9\%$ . Experimental data reveal a strong surface affinity for PI, with  $\phi_{\text{surf}} > 0.95$ , independent of temperature and film thickness at both the Si and air surfaces. This high surface composition is best modeled with a large value of  $\mu_1$ . We chose the value of  $\mu_1$  to be 0.5 and treated the surface interaction to be long-ranged. The average composition of PI was set to 0.55 as reported in the work by Grull et al.<sup>3</sup>

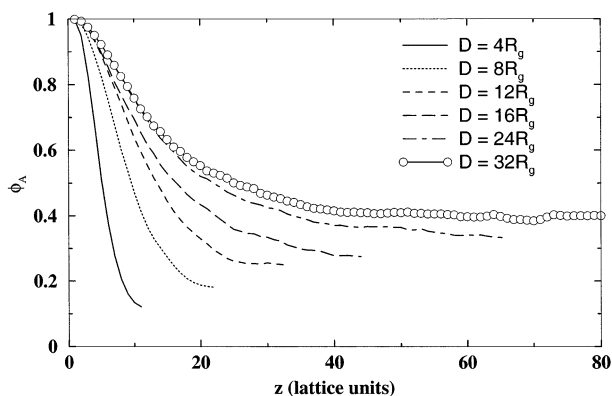
**III. Results and Discussion. Interpretation Using the Mean Field Theory.** Figure 1 compares experimentally deduced composition profiles<sup>2,3</sup> to theoretical predictions. It is evident from these plots that the mean field theory apparently reproduces the trends in the experimental profiles for 170 and 140 nm films reasonably well. However, it does not match up well in the cases of 70 and 90 nm films. In particular, neither the surface composition gradients nor the middle com-

position in the two thinnest films can be reproduced by mean field theory.

To examine this disagreement further, we note that the near-surface gradient in the experimental profiles is thickness dependent, with the gradient becoming larger with decreasing thickness. The thickest films, in fact, demonstrate a rounding of the concentration profile in the vicinity of the surface, as has been observed in more weakly segregating blends. While chain distortion has been proposed as a possible reason for this rounding, its origin is still poorly understood. The thinnest film does not show any such rounding and this functional form is purely exponential. In contrast, Figure 1 shows that the theoretical profiles for all thicknesses have a rounded form in the vicinity of the surface. This result is a direct manifestation of the divergence of  $\kappa(\phi)$  as  $\phi_{\text{surf}} \rightarrow 1$ . To satisfy eq 5 requires that  $(d\phi/dz) \rightarrow 0$  in this limit, thus yielding a “rounded” profile. Thus, the fits for the 70 and 90 nm films look much more rounded at the surface than the experimental profiles, and the conservation of mass forces the predicted middle composition to go lower than that of the experiment. Our results, in summary, lead us to believe that there is a fundamental concept that needs be incorporated into the existing theory in order to properly interpret these results.

**Is this a Deficiency of Mean Field Theory?** The first possible resolution to this disagreement between theory and experiment is that mean field theory is inadequate, especially in regimes where the interfacial width is not large relative to the sizes of the molecules in the system. To examine this possibility we have conducted simulations of polymer blends of chains of length  $N = 100$  on a cubic lattice with a coordination number of  $z = 6$ . The lattice is occupied by chain segments to 80% of its full occupancy, and we consider equimolar polymer blends. The two blend components are denoted as A and B, respectively. We preclude multiple occupancy of lattice sites and the only interactions are between nearest neighbors. We employed the following energetic interactions:  $\epsilon_{AA} = \epsilon_{BB} = -1$ ;  $\epsilon_{AB} = \epsilon_{hh} = \epsilon_{hA} = \epsilon_{hB} = 0$ . Here  $h$  denotes a hole or an empty lattice site. The blends are sandwiched between identical walls which are separated by a constant distance in the range 20–180 lattice units. (The  $R_g$  of the chains is 5.3 lattice units.) The energies of interaction between the polymer segments and the wall are short-ranged, one lattice unit in range, and assume the following values:  $\epsilon_{As} = -200$ ,  $\epsilon_{Bs} = -100$  and  $\epsilon_{hs} = 0$ . The temperature was defined as  $T^* = k_B T / -\epsilon_{AA}$ , and we used  $T^* = 85$ . The UCST for the bulk blend is  $T_c^* = 75$ , and hence, we simulate in the single phase. The systems were simulated in the canonical ensemble using the Metropolis Monte Carlo method, using reptation and local flip elementary moves.

Figure 2 shows our results for the concentration profile of the A segments as a function of film thickness. Our results show that the surface composition is  $\approx 1$  independent of film thickness, and that the gradient becomes sharper with decreasing thickness. These findings are consistent with both experiments and mean field theory and do not provide a critical means of distinguishing between them. The important point to note is that the simulation derived compositions in the middle of the film decrease monotonically with decreasing film thickness. For the thinnest film, which is  $\approx 4R_g$  in thickness, the middle composition has decreased all



**Figure 2.** Volume fraction of component A as a function of the distance from one of the bounding walls, as obtained from Monte Carlo simulations. The film thicknesses considered are shown in the figure.

the way to  $\approx 0.12$ . This finding is consistent with the mean field theory but not with experiment, where we find that the middle composition does not change with decreasing thickness. We do not analyze these results further, but we note that the disagreement between theory and experiment does not appear to be a failing of the mean field theory but instead reflects some other physics not employed in this model.

**Consequence of Using Opposing Short-Ranged and Long-Ranged Surface Potentials.** Another scenario that could reproduce the large surface composition gradients in the experimental profiles of the thinner films is if the surface free energy is comprised of two parts: a short-ranged part which favors PI at the surface, and a long-ranged van der Waals part repulsive for PI. There is no stability issue [toward dewetting] in using such a form of the surface potential, since it can be shown that, if both dPB and PI are individually stable under confinement, the blend film will be stable for all compositions considered. We have calculated composition profiles for this form of the surface interaction for a range of film thicknesses. While the use of such a form sharpens the composition profile as found for the thinnest films, the composition gradients at the surface do not vary significantly with film thickness. In this sense this approach does not capture experimental trends. Moreover, the experimental trends in the middle composition as a function of film thickness were not captured and trends akin to the earlier theoretical predictions were recovered. Hence, this surface potential model cannot explain the experimental trends.

**Consequence of Using a Thickness Dependent  $\chi$  Parameter.** A possible resolution to the disagreement between theory and experiment is to assume that  $\chi$ , the Flory interaction parameter, is thickness dependent. We are motivated by theoretical findings which suggest that confinement strongly affects phase diagrams, and hence we “fit” the theoretical predictions to the experiments by varying  $\chi$ . We found a satisfactory fit for all thicknesses, and the resulting values of  $\chi$  are strongly negative, e.g.,  $-0.001$  for  $D = 70$  nm. While this result appears reasonable, we note that it is not consistent with the previous experimental work for the following reason. A negative  $\chi$  would suggest that the phase diagrams of these blends are shifted dramatically on confinement. However, experimental data on this system and on several other blends unequivocally show that the thin films phase separate within 10–15 K from their bulk binodals.<sup>5,12–17</sup> Consequently, it appears

physically unreasonable to let  $\chi$  assume a strongly negative value. A second, related point is that theories that predict large phase transition shifts on confinement assume that the  $\chi$  values are equal to the bulk values and that the shifts come from other factors such as the presence of a surface field<sup>4</sup> and the presence of gradients in the film.<sup>4,18,19</sup> The absence of practically any shifts in the phase diagram not only suggests that  $\chi$  cannot change dramatically on confinement but also suggests that some other factor overcomes the effects present in the theories.

**A Conjecture: The Role of Adsorbed Layers.** It is apparent from the earlier discussion that the mean field theory alone cannot satisfactorily reproduce the composition profiles in strongly segregating blends, especially those of thickness  $< 10R_g$ . Previous work on the transport of polymers near hard surfaces and near the air surface<sup>20–25</sup> have suggested that the presence of surfaces serves to slow chain dynamics. Pu et al.<sup>23</sup> showed that the diffusion coefficient of chains is 3–4 times smaller than that of the bulk within a distance of  $4R_g$  from the free surface even though segmental dynamics are faster. Furthermore, these workers also suggest the existence of a  $\approx R_g$  thick “gel” layer at the hard surface where chains are effectively frozen. The presence of these adsorbed layers also have measurable consequences on the spreading of polymer drops on surfaces<sup>26,27</sup> and on the forces between plates immersed in polymer melts.<sup>28,29</sup>

On the basis of these ideas we postulate that the surface segregation layers are comprised of two pieces: one near the wall which is essentially pinned, and a second layer which corresponds to the “weak” segregation of polymer to this pinned polymer layer. The form of the pinned surface layer is described by a simple form which appears to fit simulation data

$$\phi_{\text{ads}}(z) = \exp\left[-\frac{z^2}{(R_g/2)^2}\right] \quad (7)$$

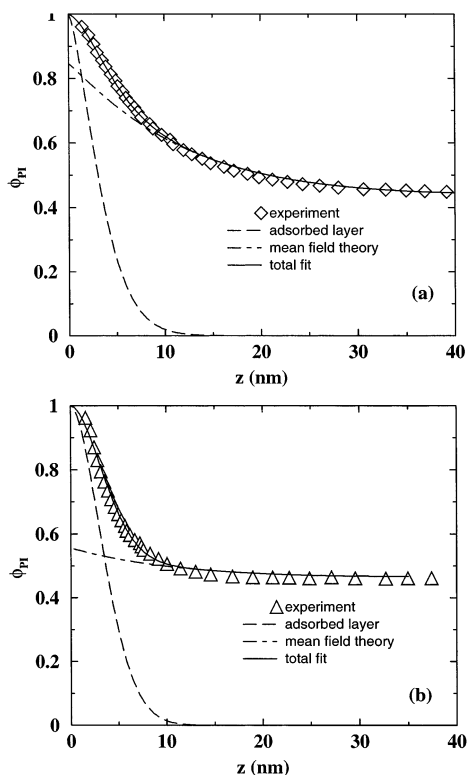
Thus, the total composition can now be mathematically expressed as

$$\phi(z) = \phi_{\text{ads}}(z) + (1 - \phi_{\text{ads}}(z))\phi_{\text{mf}}(z) \quad (8)$$

where  $\phi_{\text{mf}}(z)$  is the value of composition profile as predicted by mean field theory. Figure 3 shows that there is excellent agreement between the resulting fits and experiment. Note that the thickness of this “adsorbed” layer remains the same in both the 70 and 90 nm films. Moreover, the film interior follows the weak segregation ideas of Hariharan et al.<sup>1</sup> in that the internal profile flattens with decreasing film thickness. However, weaker surface potential parameters have to be used to fit the interior portions of the profiles reasonably well, with the  $\mu_1$  values for the 70 nm and 90 nm cases being 0.04 and 0.005, respectively. These values are 1–2 orders of magnitude lower than those ( $\mu_1 = 0.5$ ) of the thickest films. It is unclear at this time why the surface potential has to be a function of film thickness for thicknesses  $< 10R_g$ . However, since we have postulated that the behavior of polymer chains at strongly attractive surfaces is dominated by nonequilibrium effects,<sup>30,31</sup> it is very difficult to interpret this behavior using equilibrium thermodynamics.

**Connections to Results from Thicker Films.** A more careful examination of the thicker films shows that





**Figure 3.** Comparison of the experimental composition profiles with mean field theory predictions (using a variable surface energy parameter) coupled with an immobile adsorbed layer picture. Plots a and b correspond to film thicknesses of 90 and 70 nm respectively.

there are systematic differences between the mean field theory [which does not account for adsorption effects] and the experiments. The theory underpredicts the profiles about an  $R_g$  from the surface. Thus, even though the mean field theory appears to provide a good fit in the thicker films, a closer examination shows that there are probably the same discrepancies between theory and experiment seen in the thinner films. However, the thinner films show these effects in a more magnified manner.

#### Consequences of the Strongly Adsorbed Layer.

The shape of the profile, which is a direct result of bulk thermodynamics, is a direct indication of the thin film phase behavior. The critical temperature is directly tied to the value of  $C_m$  in eq 1. Using a constant surface composition and trying to fit the whole profiles using the mean field theory (without a pinned layer) would result in  $C_m$  increasing dramatically with decreasing film thickness. This leads to a large predicted shift in the critical temperature of the blend phase diagram in the thinner films. However, the thicker films, i.e.,  $D = 140$  nm and  $D = 170$  nm, show very small shifts even in this case. In contrast, the fits to the two layer model suggest that the film interior in the thinnest films is associated with small  $C_m$  values, comparable to those found for the thicker films ( $\sim 10^{-4}$ ), indicating a small change in the critical temperature in all cases. This small change in the phase behavior is consistent with recent small-angle neutron scattering (SANS) experiments<sup>32</sup> in which the blend phase diagram was found to be independent of film thickness.

**IV. Conclusions.** Using conventional mean field theory, we have demonstrated that, in films where strong surface segregation is observed, the theoretical

predictions do not satisfactorily reproduce the experimental behavior in films of  $D < 10R_g$ . Since relatively satisfactory fits are obtained for thicker films, we deduce that these discrepancies are not simply a failing of mean field theory. In the case of the thinner films, the composition profiles only appear to be fit if a strongly adsorbed layer that is about an  $R_g$  thick is postulated. These surface layers are almost immobile in the time scales relevant to experiments and thus do not respond to the changes in the thermodynamics of the film interior. Thus, in this scenario, the adsorbed layers act as “pseudo” surfaces for the unadsorbed chains, and the segregation behavior in films of  $D < 10R_g$  is greatly affected by it.

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