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Effect of long-range forces on surface enrichment in polymer blends

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Model calculations are made of surface segregation profiles for polymer and oligomer blends, both for the case in which surface segregation is driven purely by short-range forces, and for the case in which long-range (dispersion) forces are important. As expected, the inclusion of long-range forces affects the profiles as complete wetting is approached, but the effect on the shape of the surface segregation profile for a high polymer blend in the one phase region of the phase diagram is small; recent discrepancies between theory and experiment cannot be accounted for by this explanation.

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The surface of a mixture of two polymers is expected to be enriched in the component of lower surface energy; this phenomenon may be important in a variety of practical applications and a number of experimental [1–5] and theoretical [6–10] studies have recently appeared. In most cases experiments have been interpreted in terms of a van der Waals–Cahn square gradient theory [11] in which one writes down a free-energy functional of the concentration profile with depth from the surface, incorporating the chain connectivity constraint by means of a free-energy term (of entropic origin) proportional to the square of the concentration gradient. When the effect of a surface is included by means of a term which is a function solely of the surface volume fraction, the resulting functional can be minimized to yield the equilibrium surface volume fraction; the actual enrichment profile can then be simply calculated by quadrature. This theoretical approach is straightforward and recent experiments can by and large be convincingly interpreted in this framework. One particularly powerful experimental technique is provided by neutron reflectivity [12]; this technique allows a very detailed comparison of the shape of the near surface depth profile to be made with theoretical predictions. In recent experiments small but experimentally significant discrepancies between the profile shape predicted by the square gradient theory and that experimentally measured have been found [3,13]. One candidate for the origin of these discrepancies is the fact that the differences in surface energy that lead to surface enrichment have their origin in van der Waals forces, which, in contrast to the δ-function surface interaction assumed in the usual theories, are of long range. Chen, Noolandi, and Izzo [10] argued on the basis of a perturbation approach that the effect of long-range forces at the surface could indeed account for these discrepancies. In this Brief Report I describe the result of explicit numerical calculations to explore the effect of long-range forces on enrichment profiles in polymers. The conclusion is that, although there are circumstances in which long-range forces are expected to have significant effects on enrichment profiles, in the particular case discussed they are not of significant importance and cannot account for the discrepancy between theory and experiment.

As in the previous treatments [6,7,10] one starts by writing down the free energy per unit surface area $\mathscr{f}$ as a functional of the volume fraction $\phi(z)$, a function of the depth z from the surface,

$$\frac{\mathscr{f}[\phi(z)]}{kT}=\int_0^\infty dz\left[G(\phi)+\frac{a^2}{36\phi(1-\phi)}\left[\frac{d\phi}{dz}\right]^2-w(z)\phi\right]+f_s(\phi_1)\ . \tag{1}$$

Here $G(\phi)$ is the free energy of mixing which is assumed in the calculations to have the Flory-Huggins form

$$G(\phi)=\frac{\phi}{N_A}\ln\phi+\frac{1-\phi}{N_B}\ln(1-\phi)+\chi\phi(1-\phi)\ , \tag{2}$$

where N_A and N_B are the degrees of polymerization of each component, χ is the Flory-Huggins interaction parameter, and a is the statistical segment length. The effect of the surface can be represented either by a short-range interaction, $f_s(\phi_1)$, which is a function solely of the volume fraction at the surface, ϕ_1, or by a long-range interaction $w(z)$, of the type introduced by Chen, Noolandi, and Izzo [10].

The short-range energy term can be written

$$f_s(\phi_1)=-\mu_1\phi_1-\frac{g}{2}\phi_1^2\ , \tag{3}$$

where μ_1 is a chemical potential favoring one component at the surface, and g expresses the way interactions between the components are modified by the surface. In many cases, g is small compared to μ_1 [14], and in these circumstances $f_s(\phi_1)$ may be simply written as $f_s(\phi_1)=-\mu_1\phi_1$, where μ_1 can now be identified with the surface free-energy difference between the components $\Delta\gamma$, expressed in units of kT for a site on the Flory-Huggins lattice.

However, the surface energy of nonpolar liquids, including polymers like polystyrene, arises from intermolecular van der Waals forces rather than short-range surface interactions, and may be calculated to a reasonable degree of accuracy simply as half the work done in separating two half planes to infinity. This leads to an expression for the surface energy γ,

$$\gamma = \frac{A}{24\pi h_0^2} , \tag{4}$$

where A is the Hamaker constant, and h_0 is a cutoff, whose value is rather less than an intermolecular center-to-center distance. It turns out that the surface energies of a large number of nonpolar liquids are successfully predicted using a universal value for the cutoff of 1.65 Å [15], and this is the value that will be used in all calculations. Using the standard result for the van der Waals force between a half-infinite plane and a thin sheet we can write $w(z)$ as

$$w(z)dz = -\frac{\Delta A}{6\pi z^3} dz , \tag{5}$$

in terms of ΔA, the difference in Hamaker constants between the two pure materials. Assuming that h_0 is constant (this amounts to assuming that the contribution to the difference in surface energy of the difference in Hamaker constants dominates any contribution due to compressibility differences), we can use Eq. (4) to rewrite this in terms of the difference in surface energy $\Delta\gamma$, leading to the following expression for $w(z)$:

$$w(z) = -\frac{2h_0^2 \Delta\gamma}{z^3} . \tag{6}$$

Minimization of the functional of Eq. (1) leads to a differential equation,

$$\frac{d}{dz}\left[G(\phi) - G(\phi_\infty) - \frac{a^2}{36\phi(1-\phi)} \left[\frac{d\phi}{dz} \right]^2 \right] = w(z) \frac{d\phi}{dz} . \tag{7}$$

Let us consider two extreme cases. In the first the difference in surface energy arises solely from short-range interactions. Thus $w(z)=0$, but one needs to solve Eq. (7) subject to the following boundary condition at the surface [6,7,11]:

$$\left. \frac{a^2}{18\phi_1(1-\phi_1)} \frac{d\phi}{dz} \right|_{z=0} = \frac{df_s}{d\phi} = -\mu_1 , \tag{8}$$

where $\mu_1 = \Delta\gamma$. In the second case, I assume that the surface energy difference arises entirely from the long-range van der Waals interactions; here $f_s = 0$, so the boundary condition at the surface is that

$$\left. \frac{d\phi}{dz} \right|_{z=0} = 0 , \tag{9}$$

but $w(z)$ is given by Eq. (6).

In both cases one needs to incorporate another boundary condition, that $\phi(z) \to \phi_\infty$, the bulk concentration, as $z \to \infty$. In each case I solve Eq. (7) using a shooting method, in which one integrates from $z=0$, using the boundary condition given by Eq. (8) or (9), varying the values of ϕ_1 until the boundary condition at $z=\infty$ is matched. Here a fourth-order Runge-Kutte method with variable step size [16] is used.

As an illustrative calculation, consider a symmetric polymer mixture, both components of which have degrees of polymerization $N = 10^4$, with a Flory-Huggins interaction parameter of 1.5×10^{-4} (close to the value expected for polystyrene/deuterated polystyrene at 180 °C [17]), and a statistical step length of 6.7 Å (the value for polystyrene). The difference in surface energy $\Delta\gamma = 0.02$ Å [2]. This case is similar to, though not identical with, that considered in Ref. [3]. Figure 1 shows the results of the calculations assuming that the surface energy difference has its origin either entirely from long-range forces or entirely from short-range forces. The two curves are virtually indistinguishable, except very close to the surface (see the inset), where the gradient of the volume fraction does go smoothly to zero at the surface when long-range forces dominate, rather than remaining at a finite value, as expected for the case of short-range forces. This finding is in agreement with the qualitative conclusions of Ref. [10]. However, the magnitude of this effect is small and the gradients become essentially equal after a few angstroms. It seems unlikely that any experimental technique could distinguish between these two profiles, nor can one rely on a continuum theory of this type quantitatively to predict such small effects on such a small length scale. Thus the long range of the forces responsible for surface segregation phenomena in miscible blends of polymers of a high degree of polymerization seems unlikely to have an experimentally detectable effect, and the computationally much simpler short-range force approximation may be used with confidence for these cases. The reason for this is essentially the very long range of the profile, which is fixed by the connectivity of the chain.

One might expect the situation to be rather different for the case of shorter chains, whose radius of gyration is

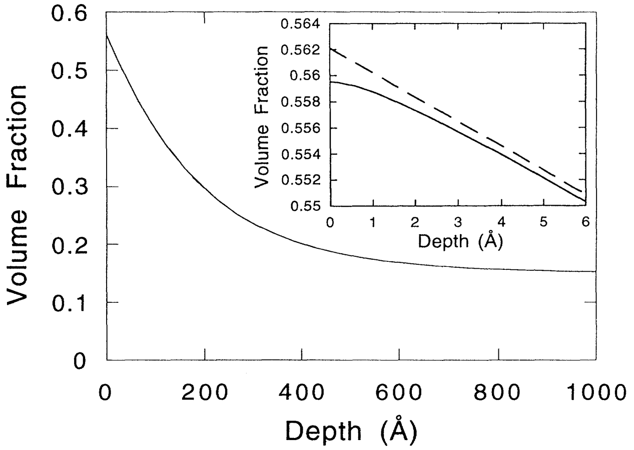

FIG. 1. Calculated surface enrichment profiles for a symmetric polymer blend of degree of polymerization $N = 10^4$ and $\chi = 1.5 \times 10^{-4}$, with a bulk volume fraction 0.15. The difference in surface energy $\Delta\gamma = 0.02$ Å; curves are shown both for the case where the surface energy difference arises from short-range forces alone (dashed line), and the case where the surface energy difference is due to a long-range van der Waals interaction (solid line). The difference between the curves is visible only in the enlargement of the near surface region in the inset.

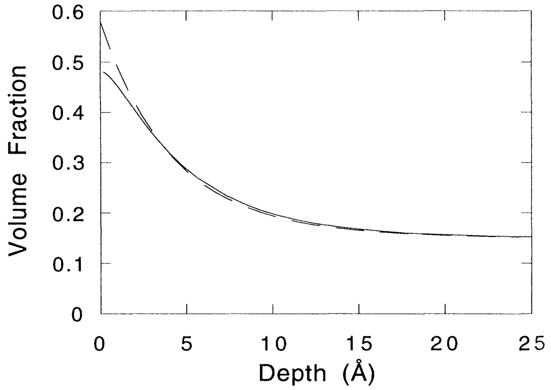

FIG. 2. Calculated surface enrichment profiles for a symmetric polymer blend of degree of polymerization $N=10$ and $\chi=1.5\times10^{-4}$, with a bulk volume fraction of 0.15. The difference in surface energy $\Delta\gamma=1$ Å; curves are shown both for the case where the surface energy difference arises from short-range forces alone (dashed line), and the case where the surface energy difference is due to a long-range van der Waals interaction (solid line).

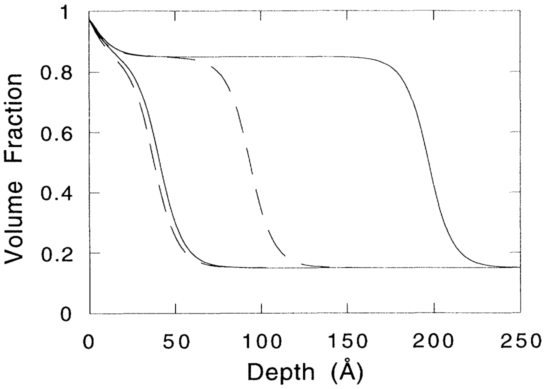

FIG. 3. Calculated surface enrichment profiles for a symmetric polymer blend of degree of polymerization $N=10$, bulk volume fraction 0.15, and difference in surface energy $\Delta\gamma=1$ Å. The left-hand pair of curves is for $\chi=0.2470$ and the right-hand pair for $\chi=0.2478$. In each case the dashed line assumes a short-range interaction, and the solid line assumes a long-range interaction.

smaller. To illustrate this, I calculate surface segregation profiles for an oligomer of degree of polymerization 10. Again I take $\chi=1.5\times10^{-4}$, but I assume a much larger surface energy difference of $\Delta\gamma=1$ Å, in order for the system to show significant amounts of surface segregation. Figure 2 shows the curves calculated with and without long-range interactions. Once again with long-range interactions the gradient of the curves go to zero at the surface, and the gradients once again become essentially equal after 2 Å. However, as the characteristic size of the segregation profile is itself only of the order of a few angstroms, the difference between the curves is significant.

As the composition or temperature is changed to approach the value on the coexistence curve, the surface excess increases until a point at which an incipient phase of lower surface energy is formed at the surface; this is separated from the bulk by an interface at a distance l from the surface [11]. As one approaches the coexistence curve l diverges; one has achieved the situation of complete wetting (this assumes that one is above the wetting transition temperature, and that there is no intervening prewetting transition—both assumptions hold for the set of parameters used here). Depth profiles are computed for the case of an oligomer with $N=10$, and a bulk volume fraction of 0.15. For this case the value of χ on the coexistence curve is $\chi=0.248$. Figure 3 shows the calculated profiles, again taking $\Delta\gamma=1$ Å, for values of the Flory interaction parameter of $\chi=0.247$ and 0.2478. It is in this situation that the presence of long-range forces results in a substantial difference in the calculated profiles; for cases approaching complete wetting the distance l characterizing the size of the wetting layer is greater for the case of long-range forces than the short-range force case, and the closer one is to coexistence (and thus the larger the wetting layer) the larger the difference. This is in accord with a well-known asymptotic result: that the divergence of the distance l with the difference in chemical potential from its value at coexistence $\Delta\mu$ is logarithmic for the case of short-range forces, but goes as $\Delta\mu^{-1/3}$ when (nonretarded) van der Waals forces are considered [18].

In summary, the effect of long-range forces on the segregation profiles of polymers and oligomers has been considered, both in the one-phase region of the phase diagram, and as the coexistence curve is approached. For oligomers the inclusion of long-range forces results in a significant change of the shape of the enrichment profile as calculated by mean-field theory, as well as a change in the size of a wetting layer as the coexistence curve is approached. For high polymers in the one-phase region of the phase diagram, in contrast, the change in shape of the segregation profile is likely to be experimentally undetectable. The cause of recent discrepancies between theory and experiment [3,13] needs to be sought elsewhere.

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