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Effect of van der Waals surface interactions on wetting transitions in polymer blends

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We examine the effect of van der Waals type interactions between the surface and monomers on wetting transitions in polymer blends. Using a Monte Carlo method we find that as long as the effective range of the van der Waals interaction is much smaller than the size of the polymers the transition may be described by a short range model. However, when the range of the interaction becomes comparable to the polymer size it can affect both the polymer density profile and the order of the wetting transition. [S1063-651X(96)05809-6]

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I. INTRODUCTION

There have recently been a number of theoretical studies [1–6] that investigate the order of wetting transitions in polymer blends at a solid surface that favors one of the phases in the blend. If the width of the thin (microscopic) wetting film that forms at the solid surface increases uniformly to a thick (macroscopic) layer the transition is commonly referred to as second order, while if this increase has a jump it is termed first order. In these theoretical studies [1–6] it is assumed that the interaction between the solid surface, or wall, and the monomers may be adequately described by a short range model. For example, in the mean field study of Schmidt and Binder [1] the perturbing effect of the wall is modeled by an additional contribution to the free energy called the ''bare surface free energy.'' The bare surface free energy is given by

$$f_s^b(\rho_1) = -\mu_1\rho_1 - \tfrac{1}{2}g\rho_1^2, \tag{1}$$

where ρ_1 is the concentration of the preferred phase at the wall, μ_1 is the surface chemical potential difference, and g represents the change in monomer-monomer interactions due to the wall.

However, the surface interaction between the monomers and the wall arises not only from short range interactions but also from van der Waals type interactions due to dipole-dipole forces between molecules in the walls and the monomers. Chen, Noolandi, and Izzo [7] and Jones [8] used mean field methods to investigate how the surface enrichment profile was modified in the presence of the van der Waals interactions. In both studies a potential of the form

$$v(z) \propto \frac{1}{z^3} \tag{2}$$

was used to represent the van der Waals interaction. Here z represents the distance from the wall to the monomer. This potential is given by the integral of the attractive part of the Lennard-Jones potential over the area of the walls. While Chen, Noolandi, and Izzo [7] suggested that the presence of these interactions could account for the discrepancy between experimentally measured results [9] and theoretical results [1], Jones [8] concluded that they could not. From studies of simple fluids [10], it has been shown that the presence of van der Waals interactions can change the order of the wetting transition. Thus it is certainly valuable to study the effect of these interactions on polymer blends. Numerical simulations using microscopic models provide an efficient method for such a study.

Here a Monte Carlo technique is employed to study the problem. The bond fluctuation model [11] is used to simulate polymer chains on a simple cubic lattice of dimension $L\times L\times H$. The polymers can interact with the walls of size $L\times L$ located at $z=0$ and $z=H+1$ and with other polymers. We consider a symmetrical mixture with each chain having N monomers. Polymers are either of type A or type B with an interaction energy given by

$$E = -\epsilon\sum_{i\neq j}\phi_i\phi_j - \epsilon_w\sum_i \phi_i\delta(\phi_i-1)v_i(z), \tag{3}$$

where ϕ_i is the occupation variable of site i (A: monomer, $\phi_i=-1$; and B: monomer, $\phi_i=1$), ϵ is the monomer-monomer interaction, and ϵ_w is the magnitude of the wall-monomer interaction at the wall. The van der Waals interaction is given by

$$v_i(z) = \begin{cases} 1 & \text{if } z \leq \sigma_s \\ (\sigma_s/z)^3 & \text{if } z > \sigma_s, \end{cases} \tag{4}$$

where ϕ_s is a range parameter for the interaction. A large σ_s corresponds to an interaction that can be felt a long way from the wall. Note that we only consider a short range interaction between monomers; i.e., only monomers that are less than three units apart are considered to have a nonzero interaction energy. Since it is known that the van der Waals interaction between monomers decays much more rapidly than in Eq. (4) (i.e., the exponent is 6 rather than 3) we feel this assumption is justified. We also use a short range model to compare results. This model is given by Eqs. (3) and (4) but with the restriction that $\sigma_s=1.0$ and for $z>1.0$ the interaction is zero. We initially fill the lattice with the A-phase polymers up to a volume fraction of 0.5, which represents a dense polymer melt. We then increase the surface chemical potential μ_1

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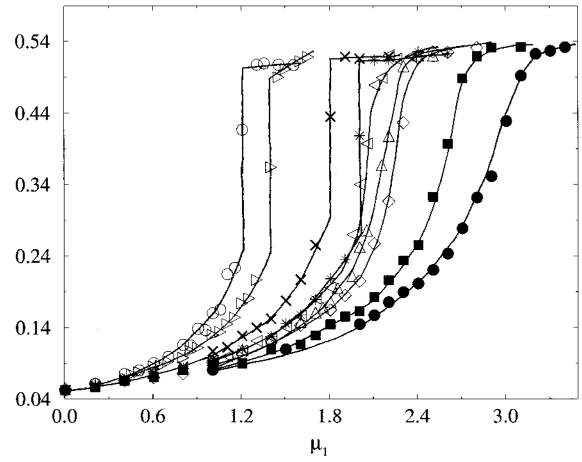

FIG. 1. *B*-phase density at the walls for a number of different range parameters, short range (●), $\sigma_s=1.0$ (■), $\sigma_s=1.3$ (◇), 1.4 (△), 1.47 (◁), 1.5 (★), 1.7 (×), 2.0 (▷), and 2.4 (○). Curves are only drawn as guides for the eye.

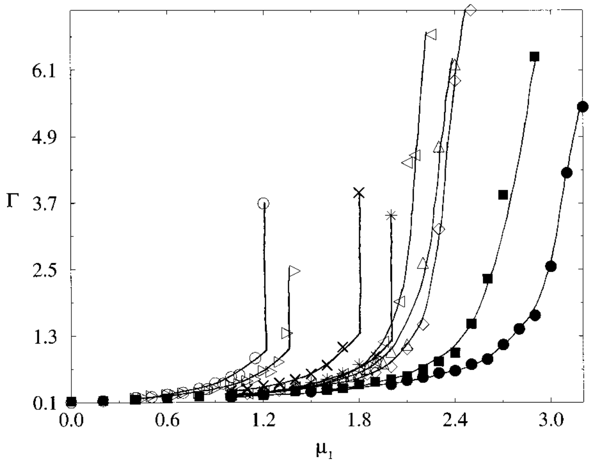

FIG. 2. Surface excess density for a number of different range parameters, short range (●), $\sigma_s=1.0$ (■), $\sigma_s=1.3$ (◇), 1.4 (△), 1.47 (◁), 1.5 (★), 1.7 (×), 2.0 (▷), and 2.4 (○).

($=\epsilon_w/\epsilon$) in favor of the *B*-phase polymers. The *B*-phase density profile ρ_B is then given by

$$\rho_B(z+1/2)=\frac{2}{L^2}\langle N_B(z)+N_B(z+1)+N_B(H-z)+N_B(H-z+1)\rangle, \tag{5}$$

where the angular brackets denote a Monte Carlo average and $N_B(z)$ is the number of *B*-phase monomers in the plane z lattice spacings from the wall at $z=0$. Since both walls have the same interaction the density is symmetrical about $z=H/2$. Due to the fact that in the bond fluctuation model no two monomers can be less than two lattice spacings apart, we average the density over two adjacent layers. We denote the density of the *B* phase in the layers adjacent to the walls $\rho_B(3/2)$ by ρ_1. We also calculate the surface excess density Γ, given by

$$\Gamma=\sum_{z=1}^{H/2}[\rho_B(z+1/2)-\rho(\infty)], \tag{6}$$

where $\rho(\infty)$ is the *B*-phase density in the layers in the middle layers of the lattice, or the bulk density. The surface excess density is a measure of the thickness of the wetting film. An important consideration in carrying out the simulations is how large H has to be to simulate a bulk system. To do this we have carefully monitored the density in the middle layers of the lattice and ensured that this density does not vary during the simulation. Consequently we can be sure that the results are indicative of a bulk system and so the walls may be considered infinitely far apart. Further details of the simulation technique may be found in Ref. [6].

Figures 1 and 2 show the results for the case $N=5$ and $k_BT/\epsilon=8$ for a variety of range parameters σ_s. For this simulation we used lattices of dimension $L=90$ and $H=60$. (Note for all the figures in this paper the quantities plotted are dimensionless.) The rightmost curves correspond to the short range model. It is known from previous work [6] that for the short range model simulated here, a second order transition is always obtained. For the smaller values of σ_s we still obtain a continuous increase in both ρ_1 and Γ. As the value of σ_s is increased, the nature of the transition changes. For the larger values of σ_s, both ρ_1 and Γ exhibit a finite jump at the wetting transition point μ_1^c. This is indicative of a first order transition. Thus by increasing the range parameter of the van der Waals interaction, the second order wetting transition changes to a first order transition. To accurately locate the point σ_s^c where the transition changes order, we have also calculated the surface layer susceptibility χ_{11}, which is just $d\rho_1/d\mu_1$. This quantity is given by the fluctuation relation

$$k_BT\chi_{11}=\frac{16}{L^2}[\langle N_B(1)^2\rangle-\langle N_B(1)\rangle^2]. \tag{7}$$

For a second order transition, χ_{11} increases smoothly up to its maximum value at μ_1^c. As σ_s increases to σ_s^c this maximum value increases. In mean field theory at the tricritical point [1], where the transition changes from second order to first order, $\chi_{11}^{-1}=0$. For a first order transition χ_{11} exhibits a δ-function jump at μ_1^c [1]. In the neighborhood of the tricritical point, on the second order side, we therefore numerically observe a rather sharp maximum in χ_{11}, which is a precursor of the critical divergence at σ_s^c. (See Fig. 3.) By carefully analyzing ρ_1, Γ, and χ_{11} we estimate the value of σ_s^c for the case $N=5$ and $k_BT/\epsilon=8$ [$\rho(\infty)\approx0.017$] to be 1.48 ±0.02.

Now we consider how the chain size affects the order of the wetting transition. To do this we have run simulations for the cases $N=10$ (lattice dimensions $L=90$, $H=70$) and $N=15$ (lattice dimensions $L=90$, $H=90$), but we have kept the bulk concentration at 0.017. For the case $N=10$, $k_BT/\epsilon=15$ we find $\sigma_s^c=1.61\pm0.02$ while for $N=15$, $k_BT/\epsilon=21.7$ we find $\sigma_s^c=1.69\pm0.03$. Thus as the size of the polymers increases, σ_s^c correspondingly increases. This is to be expected since the perturbing effect of the wall is felt less and less as one moves further away from the surface. We have also run simulations at a lower bulk concentration of 0.004. In this case it is known [6] that the polymers are less elongated than at the higher concentration of 0.017. The val-

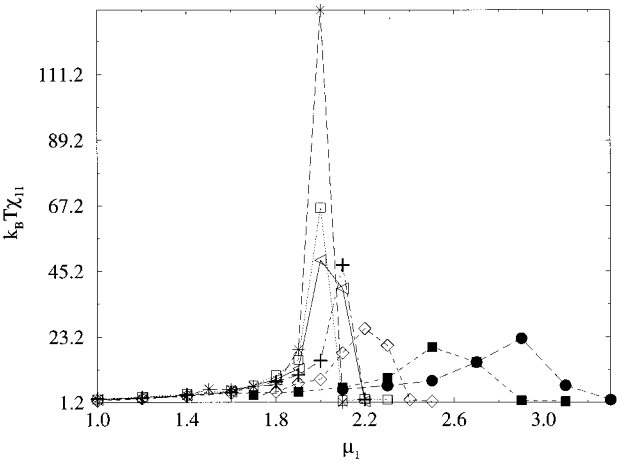

FIG. 3. Surface layer susceptibility on the second order side for different range parameters, short range (●), $\sigma_S=1.0$ (■), 1.3 (◇), 1.45 (+), 1.47 (◁), 1.49 (□), and 1.5 (★).

ues of σ_s^c at this lower concentration are estimated to be $\sigma_s^c=1.03\pm0.02$ for $N=5$, $k_BT/\epsilon=6$ (lattice dimensions $L=90$, $H=50$), $\sigma_s^c=1.10\pm0.02$ for $N=10$, $k_BT/\epsilon=11$ (lattice dimensions $L=90$, $H=60$), and $\sigma_s^c=1.23\pm0.03$ for $N=20$, $k_BT/\epsilon=20.4$ (lattice dimensions $L=90$, $H=80$).

Once again we notice that as N increases σ_s^c increases. Also the effect of decreasing the bulk concentration, or temperature, decreases the value of σ_s^c. This is because, as mentioned above, decreasing the bulk concentration causes the chains to become less elongated, on average, and so the van der Waals interaction is much more dominant than for the longer chains. Although our chains are quite short, ranging from 5 to 20 monomers only, compared to real polymer blends [8,9] where N is of the order of 10^4, we believe our results are still indicative of real systems. By this we mean that we should observe a similar increase in σ_s^c as N or T increases. In Fig. 4 a phase diagram, in the N-σ_s plane, describing the order of the wetting transition for a fixed bulk concentration is given. In a real system for a given wall-polymer pairing the range parameter of the van der Waals interaction is fixed. Given that the chain lengths are much longer than length scale of the van der Waals interaction we would expect that we would fall in the top left-hand corner of the phase diagram in Fig. 4. In this case the short range interaction should provide an adequate model for the physical interaction.

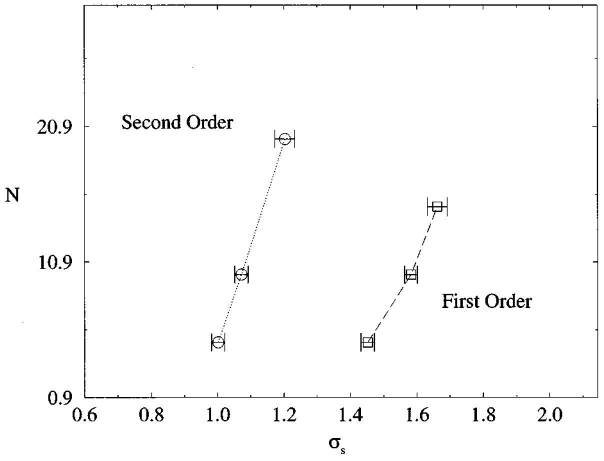

FIG. 4. Phase diagram for the wetting transition in the N-σ_s plane at a bulk density of 0.004 (○) and 0.017 (□).

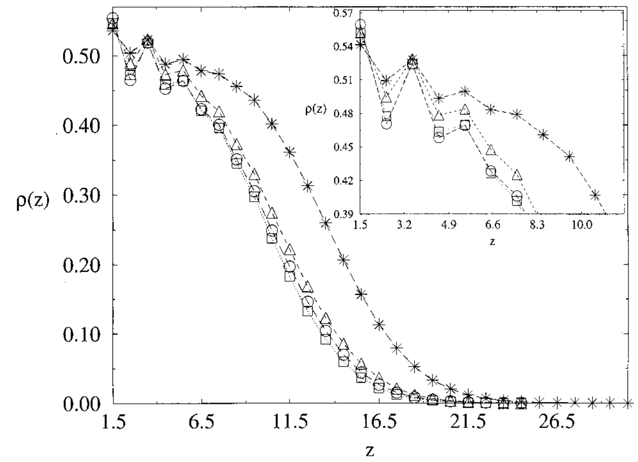

FIG. 5. B-phase density profile for various range parameters, $N=5$, $k_BT/\epsilon=6$ ($\rho_\infty=0.004$) for the short range model (○), $\sigma_S=1.0$ (□), 1.5 (△), and 2.0 (★). Inset magnifies region near the wall.

The surface enrichment profile due to the preference of the B-phase polymers at the wall is shown in Fig. 5 for a number of different range parameters. The B-phase wetting film has formed completely at the walls. In Fig. 5 the density profile is shown for the case $N=5$, $k_BT/\epsilon=6$. Far away from the wall, for all the cases, the density converges to the bulk density. Close to the wall there are oscillations in the density profiles that are due to the nature of the bond fluctuation model. These oscillations, which are also found in continuum models of hard spheres near walls and in off-lattice models of polymers, reflect the random dense packing of the monomers near the walls. For $\sigma_s=1.0$ there is not a great difference in the profile from the short range model. However, as σ_s increases it can be seen that the gradient of the density profile at the wall becomes less steep so that the profile decays more slowly than the short range model. This is more clearly seen in the inset where we magnify the region near the wall. This characteristic of the van der Waals interaction has been observed before experimentally [9] and in theoretical models [7,8]. Similar density profiles are observed for all the other chain lengths and temperatures.

It is therefore concluded from our results that as long as the effective range of the van der Waals interaction is much smaller than the size of the chains the short range model should be a good approximation to the real physical interaction between the wall and the polymers. When the range of the interaction becomes comparable to the size of the polymers there are significant deviations in the density profile near the wall. If the range of the van der Waals interaction is sufficiently large it can affect the order of the wetting transition, that is from a second order wetting transition to a first order transition. However, for experimental systems where the degree of polymerization is large, ~10^4 [8,9], we would expect the short range model to be sufficient to model the polymer-wall interaction.

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