Interfaces Between Coexisting Phases in Polymer Mixtures: What Can We Learn from Monte Carlo Simulations?

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Abstract: Symmetric binary polymer mixtures are studied by Monte Carlo simulation of the bond fluctuation model, considering both interfaces between coexisting bulk phases and interfaces confined in thin films. It is found that the critical behavior of interfacial tension and width is compatible with that of the Ising model, as expected from the universality principle. In the strong segregation limit, only qualitative but not quantitative agreement with the self-consistent field (SCF) theory is found. It is argued that the SCF theory requires $\sqrt{6\chi} << 1$ but for the short chains studied (N = 32 effective monomer units per chain), the limit is only reached for $\sqrt{6\chi}$ close to unity. Also, the effective χ-parameter decreases in the interface. It is shown that the interfacial width w does not increase by the adsorption of block copolymers as long as their areal density is still dilute ("mushroom" regime). But a broadening of interfaces does occur for thin films confined between walls at distance D, due to fluctuations that lead to $w \propto \sqrt{D}$ for short-range forces, in agreement with experiment.

INTRODUCTION

Polymer blends have many useful applications (Refs. 1,2). But since entropy of mixing in a (symmetric) polymer mixture (A,B) with chain lengths $N_A = N_B = N$ is reduced by a factor 1/N (Refs. 3-5), most polymers are not uniformly miscible under conditions of interest. Thus most blends are inhomogeneous on mesoscopic scales, containing A-rich and B-rich domains separated by interfaces (Refs. 1,2,5-7). Structural and thermodynamic properties of these interfaces are both practically relevant and an interesting problem of statistical mechanics (Refs. 5-24). For instance, the following questions arise: how do the interfacial tension σ and the interfacial width w depend on the Flory-Huggins parameter χ and the chain length N? Can one compare theoretical "intrinsic" interfacial profiles with measured ones which are broadened by fluctuations? Does the capillary wave theory account for this

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broadening? Is there an effect of confinement on w in thin films? Is w affected by the adsorption of block copolymers?

We address these problems via Monte Carlo simulation of a coarse-grained model system, the bond fluctuation model (Refs. 18,19,21,23-28) of polymer chains on the simple cubic lattice. Computer simulation of macromolecular materials is a particularly useful tool (Ref. 29) since the model Hamiltonian characterizing intrachain and interchain interactions can be fully specified and all parameters used by phenomenological theories (e.g., Refs. 8-17,20) can be explicitly determined. Thus a stringent test of the theories is possible and, in contrast to experimental tests, no adjustable parameters whatsoever are involved (Ref. 29). Note that systematic errors of simulations (equilibration, finite size effects, etc.) can be controlled for such simplified models and, apart from statistical errors, exact information for the considered model is obtained. Properties are available over a very wide temperature range (by construction, the model shows neither a glass transition at low temperatures, nor chemical degradation at high temperatures); complications, such as asymmetry between A and B, can be eliminated at a first stage (as will be done here) but can be considered at a later stage (Ref. 24). In this way, the physical origin of various complex phenomena can be nicely disentangled. These points will be exemplified in the present paper.

In the next section we introduce the model and summarize its phase behavior in the bulk. Then the temperature dependences of interfacial tension and interfacial width are presented and compared with theoretical predictions (Refs. 8,12,13,17,20). Thereafter, the effect of block copolymers adsorbed at the interface is discussed and finally the effect of confinement on interfacial profiles in thin-film geometry will be analyzed. The paper concludes with a brief outlook on experiments.

MODEL AND BULK PHASE BEHAVIOR

Polymers are represented as effective monomer units connected by effective bonds that can fluctuate in their length (Refs. 25-29), the lengths 2, $\sqrt{5}$, $\sqrt{6}$, 3 and $\sqrt{10}$ lattice spacings being permitted. Henceforth, the lattice spacing is taken as the unit of length. Each effective monomer unit blocks a cube of eight neighboring sites from further occupation, using a simple cubic lattice with a volume fraction of occupied lattice sites ϕ = 0.5, corresponding to melt densities (Ref. 27). Such a model can be

justified (Ref. 29) by integrating 3-5 consecutive C-C-bonds along the backbone of an atomistic chain model into one effective bond. Hence, using a chain length N = 32 (as done here) corresponds to a degree of polymerization of 100-160 in a real polymer. Interactions between monomer units are described by a square well potential of the range $\sqrt{6}$, choosing the most symmetric energy parameters $\varepsilon_{AA} = \varepsilon_{BB} = -\varepsilon_{AB} = -k_B T\varepsilon$.

Apart from the excluded volume, no intrachain potential is used, assuring Gaussian coil statistics (in the melt) even for very small N, i.e., the gyration radius scales as $R_g = b\sqrt{N/6}$, the statistical segment length b being 3.05 ($R_g \approx 7$ for N = 32). The Flory-Huggins parameter χ equals $2z_c\varepsilon$ (Ref. 3), where $Z_c \approx 2.65$ is the effective coordination number in the bulk (Ref. 18). Figure 1 shows the phase diagram of this symmetric model mixture, as obtained from the finite-size scaling analysis (Refs. 18, 28). The critical temperature $T_{crit} = 69.35$ °C (Ref. 28) is somewhat depressed relative to the Flory-Huggins estimate ($\chi_c = 2/N$, see Ref. 3), $T_c \approx 84.40$ °C. It can be also seen that the coexistence curve does not have the parabolic shape predicted by the mean-field theory, $\rho_A^{coex} = \frac{1}{2}\left(1 \pm \sqrt{3}\left(1 - \frac{T}{T_{crit}}\right)^{\beta}\right)$ with $\beta = 1/2$ (Refs. 3-5), but, rather, the critical behavior of the Ising universality implies

$$\rho_A^{coex} = 0.5 \pm 0.682\,(1 - T/T_{crit})^{\beta}, \qquad \beta \approx 0.324. \tag{1}$$

While for $N \to \infty$ the behavior of polymer mixtures is mean-field-like (Refs. 4,5), simulations (Refs. 28,30) and experiments (Ref. 31) have shown that one needs chain lengths at least an order of magnitude longer than those used here to see a crossover towards the mean-field behavior, which hence can be safely disregarded. Of course, a disadvantage of these short chains is that the characteristic length scales of the polymer (b, R_g, and the correlation length ξ of concentration fluctuations) are all of the same order of magnitude (e.g., $\xi = 3.5$ for $\varepsilon = 0.03$). While simulations with N = 128 are feasible in a strong segregation limit (Ref. 19), in a weak segregation limit this would require a too great computational effort.

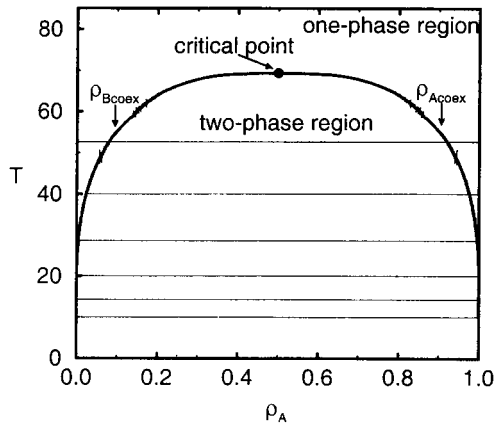

Fig. 1

Phase diagram of the symmetrical A-B polymer mixture (N = 32) with variables temperature (choosing units such as $T = \varepsilon^{-1}$, $k_B = 1$) and volume fraction. The thin horizontal lines show the temperatures where the interfacial properties were investigated (Ref. 18).

INTERFACIAL TENSION AND INTERFACIAL WIDTH

Using finite LxLxL lattices with periodic boundary conditions and applying a multicanonical (Ref. 32) algorithm in the semi-grandcanonical ensemble, one can sample the minimum $P_L\left(\rho_A^{min}\right)$ of the order parameter distribution $P_L(\rho_A)$ over a wide range of linear dimensions L (Ref. 18). It has been shown (Ref. 33) that for $L >> \xi$, the system configurations near this minimum are dominated by heterophase states, with two LxL interfaces (connected by the periodic boundary conditions) separating an A-rich domain in the center of the box from A-poor domains surrounding it (or vice versa). Therefore, the depth of the minimum is controlled by the total free energy excess due to these interfaces (Ref. 33), $P_L\left(\rho_A^{min}\right) / P_L\left(\rho_A^{max}\right) = \exp(-2L^2\sigma/T)$. This method takes all interfacial fluctuations fully into account, and does not rely on any direct observation of the interfaces.

A different strategy is needed, of course, for the study of interfacial profiles and the interfacial width w. Here we choose an LxDxL geometry, with D = 64 and L varying from 64 to 512, applying periodic boundary conditions only in the x- and z-directions, while an "antiperiodic" boundary condition in y-direction is used. That is an A(B) monomer that leaves the right boundary of the simulation volume (at y = D/2 = 32) and enters at the left boundary (at y = -D/2 + 1 = -31) as a B(A) monomer; it hence changes its identity. The same holds for movements in the inverse direction. This forces an A-B interface into the system, but does not fix its location. Before taking

"measurements", the translational invariance of the system is used to shift the interface to the center, near y = 0. We define $m(y) = 2\rho_A(y) - 1$ from the instantaneous volume fraction profile $\rho_A(y)$ and look for a position y_1 that minimizes the absolute value of the sum $|\Sigma m(y)|$ which runs from $y = y_1 - 20$ to $y = y_1 + 20$ (Ref. 18). Taking "measurements" every 10^4 Monte Carlo steps (MCS) per monomer unit, using the "random hopping" algorithm (Refs. 25-29), with total observation times between $2.5 \cdot 10^5$ MCS and $5.1 \cdot 10^5$ MCS, sufficiently accurate average profiles are obtained. These profiles are fitted by a tanh profile,

$$\rho_A(y) = \rho_0 + \Delta\rho \tanh [(y - y_0)/w], \qquad (2)$$

where $\rho_0 \approx \rho_A^{crit} = ''$, $\Delta\rho \approx \rho_{A,rich}^{coex} - \rho_{A,poor}^{coex}$, as expected from the phase diagram.

In Figs. 2 and 3, the temperature dependences of σ and w obtained in this way are shown. We note that in the strong segregation limit $\left(\rho_{A,rich}^{coex} \to 1, \rho_{A,poor}^{coex} \to 0\right)$, self-consistent field theories give (Refs. 12,13,15,20)

$$\sigma / T = \rho_m b \sqrt{\chi / 6}\,[1 - c(\chi_{crit}/\chi)], \qquad \chi >> \chi_{crit} = 2/N \qquad (3)$$

where ρ_m is the monomer unit density ($\rho_m = 1/16$ here).

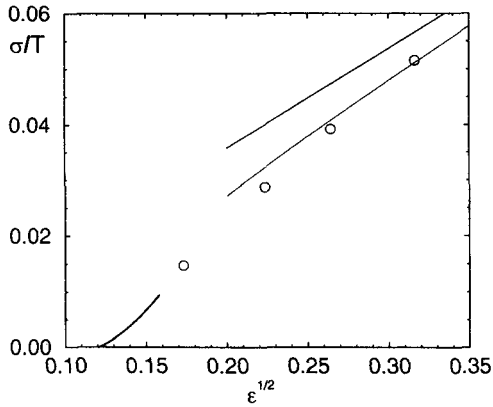

Fig. 2

Interfacial tension σ normalized by temperature T vs. $\varepsilon^{1/2}$ ($\varepsilon = 1/T$). The thick curve near the critical point shows the result of a finite-size scaling analysis: $\sigma/T = 0.0139(\varepsilon/\varepsilon_c - 1)^{2\nu}$, $\nu = 0.63$ being the critical exponent for the correlation length of the 3D Ising universality class. The straight line $\sigma/T = 0.179\varepsilon^{1/2}$ corresponds to Helfand's result in the strong segregation limit ($\chi N \to \infty$) [8]. The thin line shows corrections for the strong segregation behavior by Broseta et al., according to Eq. (3) [13]. (Taken from Ref. 18.)

The constant c of the 1/N correction is still a matter of debate (we use $c = \pi^2/12$ from Ref. 13 here). As we will see below, however, the good agreement between Eq. (3) (using c from Ref. 13) and the simulation data is somewhat accidental: all theories are assumed to be valid only for $\chi_c << \chi << 1$, and this regime is accessible only for very long chains. Thus Fig. 3 shows that w does not agree with the prediction corresponding to Eq. (3), namely (Ref. 13)

$$w = w_{SSL}\{1 + \ln 2\,(\chi_c/\chi)\}, \qquad w_{SSL} = b/\sqrt{6\chi} \quad . \tag{4}$$

Part of this discrepancy is also due to the fact that in the chosen geometry for small w, one does not observe the "intrinsic width" of the interfacial profile considered by the theory (Refs. 8-13), but rather the profile is broadened by fluctuations (see the last section). In the critical region, however, the universal constant $w^2\sigma/T \approx 0.376$ agrees with the Ising model prediction $w^2\sigma/T_c = 0.37$ (Ref. 34) or 0.416 (Ref. 35) rather well, which indicates that one does obtain roughly the intrinsic interfacial width from the simulation in the critical region.

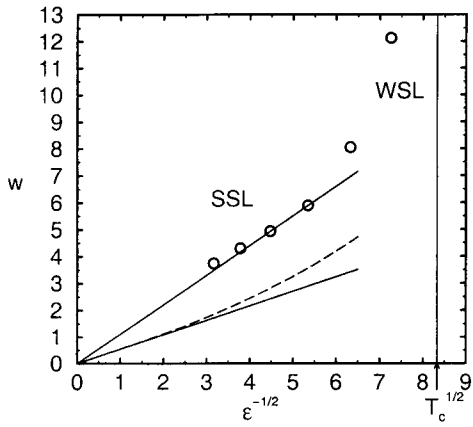

Fig. 3

Interfacial width w vs. $\varepsilon^{-1/2}$ ($\varepsilon = 1/T$). The prediction $w = 0.54\ \varepsilon^{-1/2}$ in the strong segregation limit (Ref. 8) (lower solid line) as well as the prediction of Broseta et al (Ref. 13) (dashed line) are included. The upper straight line shows a fit $w = 1.1\ \varepsilon^{-1/2}$ to the low-temperature data. The vertical line marks T_{crit}. In the weak segregation limit (WSL), the data can be fitted by a critical divergence, $w = \hat{w}(1 - \varepsilon_c/\varepsilon)^{-\nu}$ with $\hat{w} = 5.2$, $\nu = 0.63$. (Taken from Ref. 18.)

From Eq. (4), it is easy to understand the above condition ($\chi << 1$) for the validity of the self-consistent field theory: only if $(6\chi)^{-1/2} >> 1$ and w sufficiently exceeds b, the loops formed by the chains across the interface center contain many segments and hence can be treated by a continuum theory. A further effect ignored by the standard treatments is the reduction in the effective coordination number z_c and thus the

effective Flory-Huggins parameter χ in the center of the interface (Fig. 4). Thus a reliable theoretical prediction of the intrinsic interfacial width is difficult, even for our simple model where all necessary properties are known.

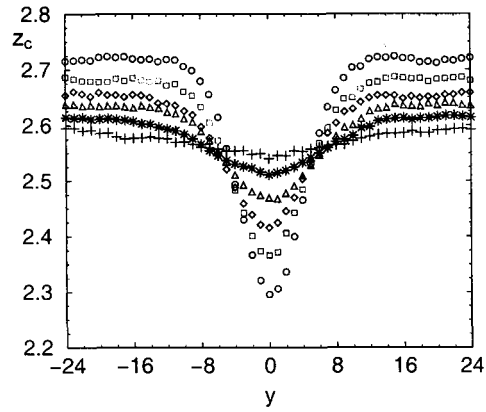

Fig. 4

Effective coordination number z_c plotted vs. the distance y from the center of the interface for N = 32 and several ε. (Taken from Ref. 18.)

o ε=0.1, □ ε=0.07, ◇ ε=0.05, Δ ε= 0.035, * ε=0.025, + ε=0.019

ADSORPTION OF BLOCK COPOLYMERS AT THE INTERFACE

It is rather popular to use block copolymers as polymeric surfactants which adsorb at the interface between coexisting phases of incompatible blends (Refs. 1,2,36), acting as compatibilizers. However, the precise mechanism of this effect is still controversial (Ref. 36). Thus it is of interest to study this problem by our model simulation, too: we can add strictly symmetric and monodisperse block copolymers $A_{fN}B_{(1-f)N}$, f = 0.5, to our A-B interface and vary all parameters of interest in a controlled fashion to study how interfacial properties are affected. Figure 5 shows, as a first step, that in the dilute regime (where the adsorbed block copolymers form "mushrooms" which do not interact with each other), the interfacial profiles of total monomer unit densities are not at all changed, in comparison to a blend at the same value of ε without any copolymers! Since under the conditions of this simulation (1024 chains out of 32 768 were copolymers), about 30% of the interfacial area is covered by block copolymers, this lack of any interfacial broadening by the copolymers is surprising. It turns out, however, that this behavior is in agreement with the corresponding self-consistent field calculations (Ref. 21), which can also account qualitatively, though not quantitatively, for most structural properties of these adsorbed block copolymers. The latter are not yet stretched chains, but rather "dumbbells" consisting of mildly perturbed Gaussian A and B coils, oriented perpendicularly to the interface.

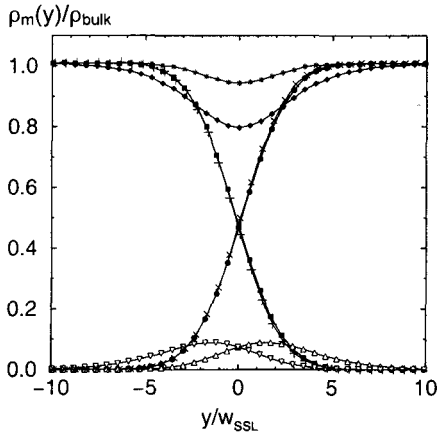

Fig. 5

Monomer unit density normalized by the bulk density, $\rho_m(y)/\rho_{bulk}$ versus y/w_{SSL}. The interfacial width in the strong segregation limit is $w_{SSL} = 1.71$ at $\varepsilon = 0.1$ (cf. Eq.(4)). Densities: total (ρ), • monomer unit A(ρ_A), ■ monomer unit B(ρ_B), ◆ homopolymers (ρ_h), Δ monomer unit A in the copolymer (ρ_{Ac}), ∇ monomer unit B in the copolymer (ρ_{Bc}), × pure homopolymer A(ρ_A^0), + pure homopolymer B(ρ_B^0). (Taken from Ref. 21.)

SIZE EFFECTS ON INTERFACIAL WIDTHS IN CONFINED FILMS

As a last topic, we consider phase coexistence of an unmixed polymer blend confined between asymmetric walls, a distance D apart, such that the left-hand wall prefers the B-rich phase, while the right-hand wall prefers the A-rich phase. For simplicity, we choose the strength of the wall interactions precisely equal on both walls, $\varepsilon_w = 0.1$, if monomers are at a distance $\Delta z \leq 2$ from either wall (which otherwise is hard and structureless). Choosing $\varepsilon = 0.03$ for $N = 32$, we are far below the critical point ($T/T_{cb} \approx 0.48$), but still above the wetting transition temperature;thus the average interface position is stabilized in the center of the film (Ref. 23). Figure 6 shows that the profile significantly depends on the film thickness. This broadening of the profile with increasing thickness results from capillary waves; the squared width w^2 becomes (e.g., Ref. 17)

$$w^2 = w_0^2 + (4\sigma / T)^{-1} \ln (q_{max}/q_{min}), \qquad (5)$$

where w_0 is the "intrinsic width" and q_{min}, q_{max} are the smallest and largest wavenumbers of capillary waves that contribute to the broadening. Taking $q_{max} = 2\pi/\xi_b$, $q_{min} = 2\pi/\xi_{\|}$ and estimating (Refs. 22,23) the correlation length $\xi_{\|}$ of interfacial fluctuations in this confined geometry as $\xi_{\|} \approx \xi_b \exp(\kappa D/4)$, where κ^{-1} is the transverse intrinsic length scale, we find

$$w^2 = w_0^2 + (16\sigma/T)^{-1} \kappa D. \qquad (6)$$

Taking for w_0 the self-consistent field (SCF) estimate and calculating κ from the theory of Parry et al. (Ref. 37), as quoted in Fig. 6, yields fair agreement with the

Monte Carlo results for large D. For small D, the observed widths fall systematically below the asymptotic estimate, Eq. (6). This happens because then the walls squeeze even the intrinsic interfacial profile.

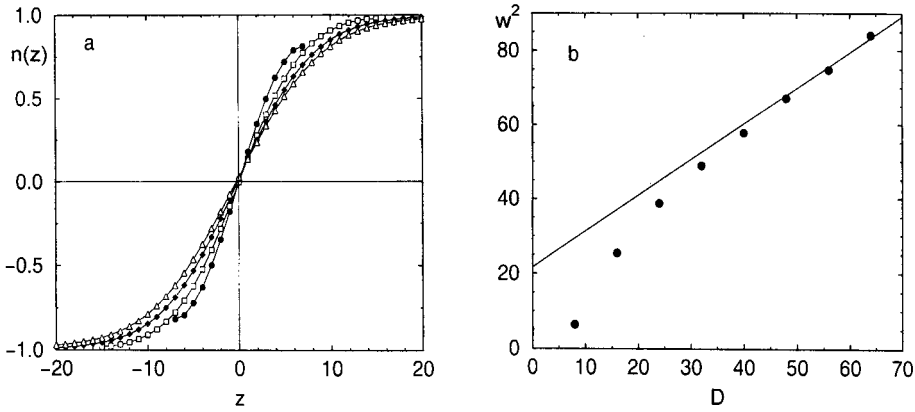

Fig. 6: (a) Order parameter profile $m(z) = (\rho_A(z) - \rho_B(z))/(\rho_A(z) + \rho_B(z))$ versus distance z from the interface center for films of various thicknesses D (lateral size L = 256, periodic boundary conditions in x,y directions). D values: ● 64, ■ 48, ◆ 32, ▲ 16. (b) Squared interfacial width w^2 versus film thickness : • MC simulation, – theoretical prediction (Eq. 16), $\kappa^{-1} = \xi_b(1 + \omega/2)$, $\xi_b = 3.6$, $\omega^{-1} = 4\pi\xi_b^2\sigma/T$, $\sigma/T = 0.015$, $w_0 = w_0^{SCF} = 4.65$). (Taken from Ref. 23.)

CONCLUDING REMARKS

In this paper, it was shown that computer simulations can yield an extremely complete description of interfaces in polymer blends: interfacial tension, interfacial profile of various densities (including particular points along the chains, e.g. chain ends and A-B bonds for block copolymers), and chain configurational properties. In the theoretical description, the SCF theory provides a useful guide in the SSL, while the full crossover to the (Ising-like) critical behavior cannot yet be described theoretically. A factor hampering comparisons of theory with both simulation and experiment is that theory always yields only the "intrinsic" profile, while observed profiles exhibit broadening by capillary-wave fluctuations. The latter are also responsible for a regime in thin films of thickness D, where the width scales as $w \propto \sqrt{D}$ for short-range wall-polymer forces. While this behavior seems to be consistent with some experiments (Ref. 22), other experiments (Ref. 38) claim that $w \propto \ln D$,

which is expected for long-range wall-polymer forces (Refs. 23,38). Still others claim (Refs. 39,40) that there is no broadening at all, and one does observe the intrinsic width in experiments, and hence only a preparation-induced "initial roughness" needs to be subtracted. More experiments are desirable to clarify this situation, and we expect that the present work will help to analyze them correctly.

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