Capillary-Wave and Chain-Length Effects at Polymer/Polymer Interfaces

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A continuum-space bead-spring model is used to study the phase behavior of binary blends of homopolymers and the structure of the interface between the two immiscible phases. Results of numerical simulations using molecular dynamics supplemented by Monte Carlo exchanges are presented. The structure of the interface is investigated as a function of immiscibility, chain length, and system size. Capillary waves are observed, and their measurements allows us to determine the surface tension. We propose a universal method of measuring the interfacial width in terms of second moments of the different contributions to the first derivative of the interfacial profile. Predictions of this method are directly verified. [S0031-9007(97)04965-X]

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The mixing of two different homopolymer species, say, A and B, in the molten state often results in a system of two immiscible phases. The structure of the interface between the phases has been the object of several theoretical studies [1,2] which use as a starting point the Flory-Huggins free energy of the blend and its well-known associated interaction parameter χ_{AB} [3]. These theories predict that the intrinsic order parameter profile of an interface located at z_0 is well approximated by [4]

$$\psi(z) = \psi_0 \tanh[2(z - z_0)/w_0], \tag{1}$$

where $\psi(z) \equiv [\rho_A(z) - \rho_B(z)]/[\rho_A(z) + \rho_B(z)]$, ρ_I is the number density of species I, and ψ_0 is the bulk value of the order parameter. According to the same theories [2], the intrinsic interfacial width w_0 is predicted to follow $w_0 = a(6\chi_{AB})^{-1/2}$, while the surface tension $\gamma = (k_B T/a^2)(\chi_{AB}/6)^{1/2}$. Here, a is the statistical segment length, k_B is the Boltzmann constant, and T is the temperature.

On the experimental side, neutron reflectivity experiments [5] have measured a value of w_0 that is systematically and substantially larger than that predicted theoretically from the χ_{AB} associated with these blends. More recent experiments [6] seem to support the proposed explanation [5] that the presence of capillary waves [7] at the interface could be responsible for this discrepancy.

Of similar importance is the effect of chain length N on the interfacial width, since theoretical treatments are mostly in the limit of infinite N. Some finite-chain-length corrections have been proposed [8], but none of these have been tested systematically.

With these motivations in mind, a simple continuous-space (CS) model has been developed [9] in order to study binary blends of homopolymers. It is the purpose of this Letter to present results, as derived from this model, for capillary-wave and chain-length effects at the interface of immiscible homopolymer blends. Our approach differs significantly from previous numerical studies which use lattice models almost exclusively [10]. For systems with interfaces, CS models have interesting features: besides their inherent spatial isotropy and the absence of pinning, they offer a simple way to determine the surface tension from the measured pressure tensor [11]. Moreover, provided the forces are short ranged, theoretical work [12] suggests that interfaces in the continuum exhibit no roughening transition.

The CS model used here has been described in more detail elsewhere [9]. In this model, the polymer chains are represented by attaching N soft spherical beads of mass m using a finitely extensible spring potential. The softness of the beads, or mers, is set by the interaction potential. A binary system is built by constructing a large number M of such chains, of given type A or B, and enclosing them in a virtual box having the desired boundary conditions.

We use molecular dynamics (MD) as the simulation algorithm, supplemented by Monte Carlo (MC) type exchanges in order to improve the sampling of phase space. The time evolution of the coordinates of all chains is resolved through Newton's equation of motion (EOM), integrated using a velocity-Verlet algorithm [13]. The motion of the chains is coupled to a heat bath acting through a weak stochastic force $\mathbf{W}(t)$ and a corresponding viscous damping term with friction coefficient Γ. Besides improving the diffusion of the system in phase space, this coupling has the practical advantage of stabilizing the numerical calculation, especially in the presence of the energy fluctuations induced by the MC exchanges. Including these terms, the EOM of mer i reads

$$m\frac{d^2\boldsymbol{r}_i}{dt^2} = -\nabla_i U - m\Gamma\frac{d\boldsymbol{r}_i}{dt} + \mathbf{W}_i(t). \tag{2}$$

The last term $\mathbf{W}_i(t)$ is a white noise having an average strength determined by temperature and the friction coefficient through the fluctuation-dissipation theorem. In the viscous drag term, Γ has to be carefully chosen to avoid overdamping so that the motion of the mers is dominated

by their inertia. Finally, the conservative force term derives from a potential energy U having two contributions: the interaction potential U_{IJ} acting between all mers, responsible for excluded volume effects, and an attractive potential holding adjacent mers along the chain U^{ch}. For the first contribution in a mixture of two homopolymer species, the interaction potential $U_{IJ}(r_{ij})$ between beads i and j of types $I, J = \{A, B\}$ separated by a distance r_{ij} is taken as the repulsive core of a central-force Lennard-Jones (LJ) 6:12 potential,

$$U_{IJ}(r_{ij}) = 4\epsilon_{IJ}\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6} + \frac{1}{4}\right], \quad (3)$$

for $r_{ij} < r_c = 2^{1/6}\sigma$ and zero otherwise. Instead of using the Lorentz-Berthelot mixing rules, we choose $\sigma = \sigma_A = \sigma_B$, and $\epsilon_{ij} = (1 + \delta_{IJ}\delta)\epsilon$, where $\delta \geq 0$ is a small parameter controlling the miscibility and δ_{IJ} is the Kronecker delta. Our choice in energy parameters can be seen as a special (symmetric) case of $\delta = [\epsilon_{AB} - \frac{1}{2}(\epsilon_{AA} + \epsilon_{BB})]/\epsilon$, which represents the kind of interactions used in simple lattice systems such as in the Flory-Huggins theory. Here ϵ and σ are, respectively, parameters fixing the energy and length scales. Accordingly, our results are reported in terms of these natural units, using $\tau = \sigma(m/\epsilon)^{1/2}$ for the time scale. All the results reported here are obtained using $\Gamma = 0.5\tau^{-1}$ at a constant overall number density $\rho = 0.85\sigma^{-3}$ (isochoric) and a temperature $T = 1.0\epsilon/k_B$. Chain size N varies from *mono*mers to *30*-mers.

Simply by varying δ, while leaving the temperature constant, one can induce a phase transition from a homogeneous blend to a system with two coexisting phases. This effect is reminiscent of what is done in recent experiments reported by Gehlsen *et al.* [14] in which the phase separation of binary mixtures is studied as a function of the difference in deuterium between two otherwise identical polymer species. Thus, in principle, the model and an MD simulation method would be adequate to study the kinetics of phase separation in binary blends. However, the time scale involved in the unmixing transition—occurring through the diffusive motion of the chains—is extremely long. To properly sample the phase space in a reasonable calculation time, we supplement the MD moves with an MC procedure relabeling the type of the homopolymer chains ($A \leftrightarrow B$) with a Metropolis transition rule [15]. Our exchange attempt rate is approximately M chains per τ [9].

Cubic simulation cells of volume $L^3 = NM/\rho$ and with full periodic boundary conditions were used to study the bulk properties of our model [9]. The equilibrium bulk order parameter $\psi_0(M, N, \delta)$ was measured for different sizes as a function of the immiscibility parameter δ. A finite-size scaling analysis [9] of our results, involving the multiple-histogram technique [16], was used to extract the critical immiscibility value $\delta_c(N)$ associated with a system of infinite size ($M \to \infty$). For $N > 2$, our data are well described by $N\delta_c = 3.40(5)k_BT/\epsilon$, clearly evidencing a $1/N$ behavior of the critical immiscibility, as predicted by the Flory-Huggins theory.

The finite-size effects on the interfacial properties of multiphase systems are not as well known as for the bulk. Capillary-wave effects [7], confinement [17], or finite-chain-size [8] corrections to properties such as the interfacial width or the surface tension are still under active investigation. We shall now address these questions.

Once the critical miscibility parameter is known, we can build antiperiodic immiscible systems (at $\delta_c/\delta < 1$) and study the interfacial properties of the model; that is, we use simulation cells having an antiperiodic [18,19] boundary condition in one direction and a volume $L^2L_\perp$, where $L_\perp$ is the length perpendicular to the interface. Figure 1 shows the interfacial profile of the order parameter $\Psi(z)$ of such systems, obtained by spatially averaging $\psi(\boldsymbol{r})$ in xy slices, perpendicular to the antiperiodic direction z, and then averaging the resulting profiles in phase space with the proper offset (since the zero of the interface is translationally invariant). It is tempting to fit the order parameter profile directly to the same intrinsic interfacial function $\Psi(z) = \psi_0 \tanh(2z/w)$, and thus associate a width w with the interface. However, our averaging of the profile incorporates the effect of the intrinsic interfacial width w_0 as well as any other perturbation broadening the interface, such as capillary waves. To separate both effects, a systematic study of the interfacial profile for different system sizes has to be performed.

In capillary wave theory [7], the roughness $\langle(\Delta z_0)^2\rangle^{1/2}$ of the zero of a sharp interface $z_0(x, y)$ is found to be, in the linearized regime of small distortions,

$$\langle(\Delta z_0)^2\rangle = \frac{k_BT}{2\pi\gamma}\ln\left(\frac{q_l}{q_L}\right), \quad (4)$$

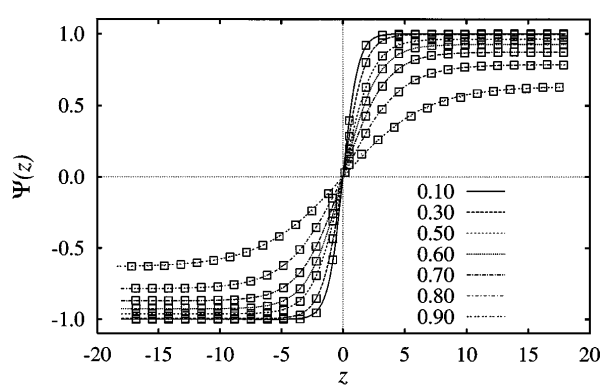

FIG. 1. The interfacial profiles $\Psi(z)$ defined as the xy-slice averages of $\psi(\boldsymbol{r})$ for a system of 4000 10-mers with antiperiodic boundary conditions. The values of δ_c/δ are as indicated. The lines are from a least-squares fit to the function $\Psi(z) = \sum_{i=1}^{2} a_i \operatorname{erf}(\sqrt{\pi}\, z/w_i)$.

where q_L is the lower cutoff driven by the system size and generally taken to be π/L while q_l is the upper cutoff, usually assumed to be driven by some correlation length such as $\pi/(c'w_0)$, where c' is some number. It is assumed here that $L_\perp \to \infty$ so that the roughness is strictly controlled by L.

We shall now derive a general and formal argument allowing us to add the roughening effects of capillary waves to the intrinsic interfacial width, which we shall measure universally as a moment. If one assumes that capillary waves can be decoupled from fluctuations in density and in order parameter, the averaged interfacial profile $\Psi(z)$ can be written as the convolution of the intrinsic interfacial profile $\psi(z - z_0)$, and the probability $\mathcal{P}(z_0)dz_0$ of finding the interface at z_0,

$$\Psi(z) = \int_{-\infty}^{\infty} \psi(z - z_0)\mathcal{P}(z_0)\, dz_0 . \tag{5}$$

By applying d/dz on each side, one finds that $\Psi'(z)$ is the convolution of two well-bounded functions, $\psi'(z - z_0)$ and $\mathcal{P}(z_0)$. We associate a functional measure $\upsilon[f]$ to a well-bounded function f as [20]

$$\upsilon[f] \equiv \frac{\int_{-\infty}^{\infty} z^2 f(z)\, dz}{\int_{-\infty}^{\infty} f(z)\, dz} = \frac{-\frac{d^2}{dk^2}\tilde{f}(k)|_{k=0}}{\tilde{f}(0)}, \tag{6}$$

where $\tilde{f}$ is the Fourier transform of f. For real f, it can be shown [21] using the convolution theorem that $\upsilon[\Psi'] = \upsilon[\psi'] + \upsilon[\mathcal{P}]$, which we rewrite as

$$\Delta^2 = \Delta_0^2 + \frac{k_B T}{2\pi\gamma} \ln\left(\frac{L}{c\Delta_0}\right), \tag{7}$$

where $\Delta^2 \equiv \upsilon[\Psi']$ now measures the total interfacial width while $\Delta_0^2 \equiv \upsilon[\psi']$ is related to the intrinsic interfacial width w_0. The last term comes from Eq. (4) and the fact that $\upsilon[\mathcal{P}] = \langle(\Delta z_0)^2\rangle$. We reiterate here that Eq. (7) is of general validity since it does not rely on any specific functional form and only uses well-controlled approximations. For example, if one fits $\Psi(z)$ to either a simple $\psi_0 \tanh[2z/w]$ or to $\sum_{i=1}^{n} a_i \mathrm{erf}(\sqrt{\pi}\, z/w_i)$ [22], then Δ^2 is $\pi^2 w^2/48$ or $\sum_{i=1}^{n} a_i w_i^2/(2\pi \sum_{i=1}^{n} a_i)$, respectively.

In Fig. 2, we present results from fitting $\Psi(z)$ to $n = 2$ error functions. The dependence of Δ^2 on both the linear size L of the system (while $L_\perp \gg \Delta$) and δ clearly evidences the presence of capillary waves. To our knowledge, this is the first time that capillary waves have been observed in computer simulations of polymer interfaces [19]. We fit our data to the expression $\Delta^2 = a_\delta + b_\delta \ln(L)$, where $b_\delta \sim 1/\gamma_L$ (subscript L indicates that the surface tension has been derived from capillary-wave effects). By measuring the surface tension γ_P independently from the difference in the pressures (obtained from the virial [13], hence the subscript P) perpendicular and parallel to the interface [11], $\gamma_P = (P_\perp - P_\parallel)L_\perp$, one gets another estimate of the surface tension, and can compare it unambiguously with γ_L [23]. Figure 3 shows the two different measures of γ for a monomeric system. For all N, our

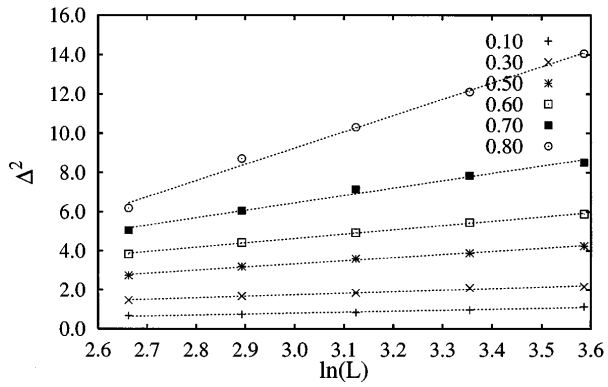

FIG. 2. Linear-size and miscibility-parameter dependence of the interfacial width for various systems of 10-mers. Values of δ_c/δ are as indicated. The lines are least-squares fits to $\Delta^2 = a_\delta + b_\delta \ln(L)$. Systems are of size $L^2 L_\perp$, with $L_\perp \gg \Delta$.

data show that with $\gamma_L = k_B T/2\pi b_\delta$ both measures are consistent, thus evidencing the origin of the broadening as being capillary waves and the validity of Eq. (7).

The other parameters a_δ obtained from the least-squares fits are always negative for the systems considered here. This is understandable given the large values of b_δ (i.e., small γ) and the fact that $a_\delta = \Delta_0^2 - b_\delta \ln(c\Delta_0)$. This last equation can be solved numerically for Δ_0 once we know a_δ and b_δ. It turns out that our data set only has a solution for $c \gtrsim 13$, thus imposing a bound on cutoff q_l. Figure 4 shows values of Δ_0 extracted by assuming $c = 13$ and plotted such as to compare with theory which predicts that $w_0^2/N \sim 1/N\chi_{AB}$, where $N\chi_{AB}$ is the measure of immiscibility in the Flory-Huggins theory [with the critical value $(N\chi_{AB})_c = 2$], such that $2/N\chi_{AB}$ corresponds to δ_c/δ for our model.

The $L_\perp$ dependence of the interfacial width has also been investigated. For $L_\perp \gtrsim 4\Delta$ (and $\delta_c/\delta \lesssim 0.8$), we find no effect of $L_\perp$ on Δ, in contrast with recent studies [17] that observed that $\Delta \sim L_\perp^{1/2}$ for near-critical

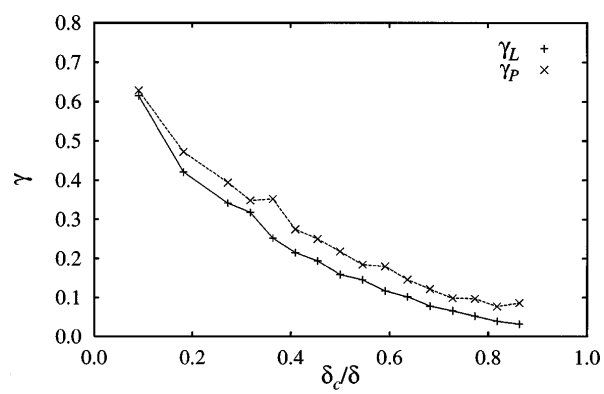

FIG. 3. Two different estimates of the surface tension for monomeric systems. Surface tension γ_P is obtained from $L_\perp(P_\perp - P_\parallel)$ while $\gamma_L = k_B T/2\pi b_\delta$, where b_δ is obtained from a plot similar to Fig. 2.

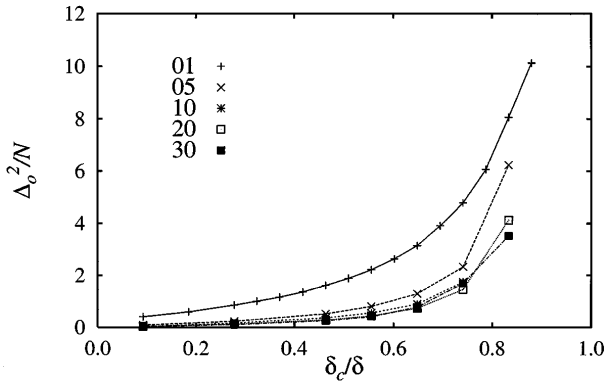

FIG. 4. The scaled intrinsic interfacial width Δ_0^2/N as estimated from Eq. (7) and $c = 13$. The chain length varies from monomers to 30-mers. The data are plotted so that the reduced miscibility δ_c/δ is equivalent for all chain lengths.

immiscibilities. In these studies, however, $L_\perp$ is such that the interface is confined so that the tails of the order parameter do not relax to the bulk value. In the present work, this effect is taken care of by using only results from systems for which $L_\perp$ is large enough so that there exists a wide region (going through the antiperiodic boundary if the interface is centered in the system) in which ψ is fully relaxed at $\pm\psi_0(\delta)$.

In Fig. 5, the effect of the chain length on the surface tension is shown. From self-consistent field results (and as $N \to \infty$), $N^{1/2}\gamma \sim (N\chi_{AB})^{1/2}$. Accordingly, our result collapses very well when $N^{1/2}\gamma$ is plotted in terms of δ_c/δ.

We have shown that a continuous-space model with a rather simple potential allows us to study the interface between immiscible binary blends of homopolymers. The natural isotropy of an off-lattice model coupled with a weak mismatch between the polymer chains made it possible for us to observe strong capillary-wave effects at the interface of moderately small systems and evaluate the surface tension unambiguously.

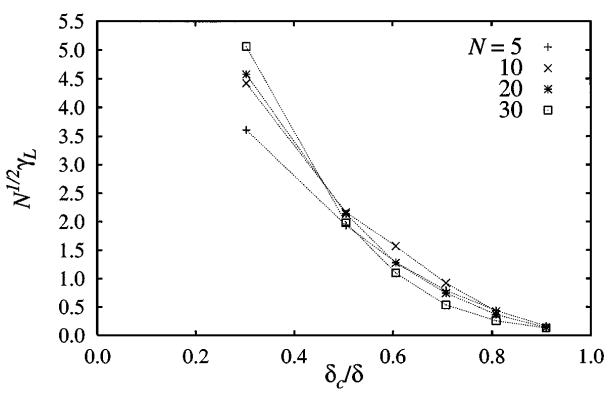

FIG. 5. The miscibility-parameter dependence of the surface tension for systems of different chain lengths. The scaling form holds very well for strongly immiscible blends and long chains ($N > 5$).

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[23] More correctly, however, γ_L is the energy per interfacial area while γ_P is the energy per cross-sectional area.