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Monte Carlo simulation of polymer mixtures: recent progress

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SUMMARY: The phase diagram of symmetrical polymer blends (A,B) confined into thin films is studied, considering both the effect of finite film thickness D and of surface forces at the confining walls that either prefer both the same species, or different species. In the case of „neutral“ walls confinement enhances the compatibility of the blend. The critical temperature is depressed, the coexistence curve gets flattened (reflecting a crossover from 3-dimensional to 2-dimensional critical behavior). But if both walls preferentially attract species A, then also the critical composition of the blend is shifted to the A-rich side of the phase diagram, and the coexistence curve exhibits a bulge just above the wetting transition temperature. If one wall attracts A and the other B, lateral phase separation sets in via a first order transition. Above this transition, an interface parallel to the walls is stabilized in the system.

Introduction and Overview

Thin polymeric films on surfaces may have many interesting applications (protective coatings, lubrication, etc.). Of course, just as one has successfully improved properties of bulk polymeric materials by producing suitable polymer blends, it is of interest to consider also thin films of polymer mixtures. The statistical mechanics of thin polymeric films, containing symmetrical polymer mixtures (A,B), are in the focus of this paper. By „symmetrical mixtures“ we mean that both chain lengths are equal ($N_A=N_B=N$) and also there is no asymmetry in chain stiffness, size of monomeric units ($\ell_A=\ell_B=\ell$), etc. We are interested in film thicknesses D larger than (but still comparable to) the gyration radius $R_{gyr}=\ell\sqrt{N}/6$.

If the lower surface of the thin film is formed by an adsorbing substrate, and the upper surface by vacuum or air, then it may happen that the thin film as a whole is unstable and decomposes into (thicker) droplets by dewetting processes etc.$^{1)}$ This situation is out of consideration here: rather we consider only two fairly idealized special cases, one case where the thin film is confined by perfectly identical hard walls, and another case where it is confined by „antisymmetric“ walls. By „antisymmetric“ we mean that one wall preferentially attracts A-monomers, while the other wall preferentially attracts B-monomers with the same strength. In both cases gradual transitions occur from a fully disordered state, where the two types of chain

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are randomly mixed throughout the thin film, to a layered structure with interfaces between A-rich and B-rich phases that run parallel to the wall. In the symmetric case, assuming that it is species A that is attracted to the wall, two A-rich layers near the walls are separated from a B-rich layer in the center of the thin film.[1,2] In the antisymmetric case, it is a single interface separating the A-rich phase on the right wall from the B-rich phase at the left wall that develops.[3-6]

We emphasize that these layered structures develop rather gradually from the corresponding surface enriched structures existing in the temperature region where the polymer mixture is compatible in the bulk, one does not encounter any sharp phase transition when one passes the critical temperature T_{cb} of unmixing in the bulk. One may encounter a critical temperature $T_c(D)$ of unmixing in the thin film but this then implies a lateral phase separation. Fig. 1 gives a qualitative description of this situation for the case of symmetric walls.

Now an interesting complication is the existence of wetting phenomena[7]: At the surface of a semi-infinite mixture being in the regime where phase separation occurs in the bulk, a macroscopically thick layer of A-rich phase may coat the surface of the B-rich phase if the surface is wet, while only atomistically thin enrichment layers exist in the nonwet state (any macroscopically extended A-rich droplet in the B-rich phase then meets the surface under a nonzero contact angle θ). Changing the temperature one may encounter a wetting transition[7], where $\theta \rightarrow 0$. In a thin film, this transition also is rounded, although remnants of it clearly can be recognized[2] (Fig. 2).

In the case of films with antisymmetric walls, the remnant of the wetting transition is an interface localization transition[8]: while for $T > T_c(D)$ the interface is almost freely fluctuating (i.e., delocalized) in the center of the thin film, for $T < T_c(D)$ it is localized at the walls. Due to the conservation of the total concentration, this localization transition again implies lateral phase separation between A-rich and B-rich domains (Fig. 3)[6]:

A particularly ideal case is the special case of films with neutral walls, for which there is neither a preferential attraction of A nor of B monomers to the walls.[9] For a mixture with critical volume fraction $\phi_{crit}=1/2$, no surface enrichment of either phase at the walls occurs. However, in the region $T<T_c(D)$ where lateral phase separation occurs[9] the minority component (A in the B-rich domains, B in the A-rich domains) is enriched at the walls, for entropic reasons.[10]

In the present paper, we shall illustrate these comments by Monte Carlo simulation results for the bond fluctuation model[2-6,9]. In Sec. 2, we shall briefly introduce the model[11,12] and discuss the effect of film thickness on the phase diagram for the case of neutral walls[9]. Sec. 3 discusses the asymmetry induced by walls that both attract the same species for a mixture whose phase diagram is symmetric in the bulk$^{2)}$. Sec. 4 presents model calculation for an interface localization transition of a symmetric polymer mixture exposed to antisymmetric walls.

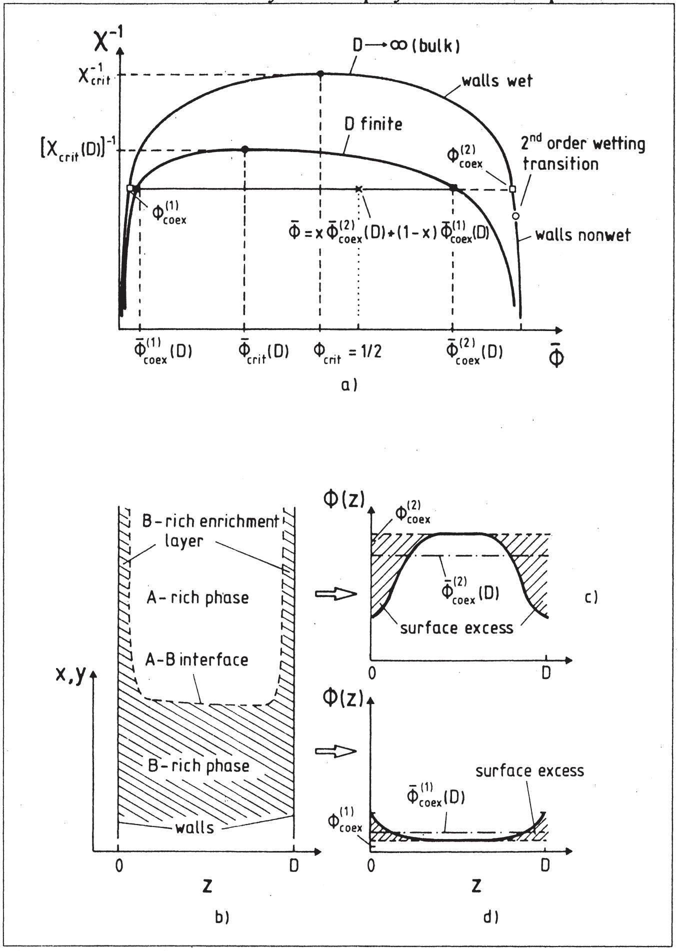


Fig. 1a) Qualitative phase diagram of a symmetrical binary (AB) mixture in both a thin film of thickness D and in semi-infinite geometry ($D \rightarrow \infty$), in the plane of variables χ^{-1} (χ is the Flory-Huggins parameter) and avarage volume fraction $\bar{\phi}$ of A in the system. Assuming a symmetrical mixture in the bulk ($D \rightarrow \infty$), the critical volume fraction is $\phi_{crit}=1/2$, and for $\chi^{-1} < \chi^{-1}_{crit}$ the volume fractions $\phi^{(1)}_{coex}, \phi^{(2)}_{coex}$ of the two coexisting phases are related by $\phi^{(2)}_{coex} = 1 - \phi^{(1)}_{coex}$. Assuming the species B is preferentially attracted to the surfaces, this symmetry relation is violated, and both the critical volume fraction $\bar{\phi}_{crit}(D)$ and the volume fraction at the A-rich branch of the coexistence curve $\bar{\phi}^{(2)}_{coex}(D)$ are shifted towards smaller values as compared to the bulk. Assuming a second order wetting transition in the semi-infinite system, this transition is rounded off in the thin film b) Schematic description of lateral phase separation for a state point inside the coexistence curve of the thin film, $\bar{\phi}^{(1)}_{coex}(D) < \bar{\phi} < \bar{\phi}^{(2)}_{coex}(D)$. c) Volume fraction profile $\phi(z)$ in the z-direction across the film, in the A-rich phase. d) Same as c) but for the B-rich phase.

Bond fluctuation model study of dimensional crossover

The bond fluctuation model uses a coarse-grained description of flexible linear polymer chains in terms of effective monomers (which block all 8 sites of an elementary cube at the simple cubic lattice from further occupation) connected by effective bonds. The length b of these bonds may take the values b = 2, $\sqrt{5}, \sqrt{6}, 3, \sqrt{10}$ (in units of the lattice spacing). Apart from excluded volume, there is a short range attraction (repulsion) between like (unlike) monomers which are no more distant from each other than $r_0 = \sqrt{6}$. In the most symmetric version of this model, these interactions are chosen as $\varepsilon_{AA} = \varepsilon_{BB} = \varepsilon_{AB} = \varepsilon T$; choosing units where $\varepsilon_{AA} = 1$ (and $k_B = 1$) ε is just the inverse temperature.

We choose a L × L × D geometry, with periodic boundary conditions in x and y directions, with two impenetrable hard walls at z = 0 and z = D+1, so layers z = 1, 2, ..., D are available for the occupancy by the effective monomers. In the case of attractive walls, an interaction of strength ε_w acts in layers 1, 2 and D-1, D respectively. (The more realistic case of a long range van der Weals type interaction with the surfaces has also been treated but will not be discussed here[4)].

The Monte Carlo simulations involve two types of moves. The first type, random hopping of effective monomers to neighboring positions and/or the „slithering snake“ algorithm, are needed to relax the local configuration of chains.[13)] In addition one uses the „identity switch“[14)], i.e. an A-chain transforms into a B-chain at fixed configuration, choosing also a factor $\exp(\Delta\mu N / k_B T)$ in the Metropolis criterion, which controls the acceptance or rejection of the attempted moves, $\Delta\mu$ being the chemical potential difference between the monomers. The simulation thus realizes the semi-grandcanonical ensemble, suitable to yield properties of pure phases in the thermodynamic limit ($L \to \infty$). In cases where one wishes to efficiently simulate phase coexistence between unmixed domains with interfaces in between, which requires a strictly canonical ensemble, a correspondingly efficient nonlocal move is the simultaneous identiy switch of two chains, A→B plus B→A, that conserves the overall composition.[6)]

In order to locate the critical temperature T_c of the model, one has to vary L over a wide range and apply finite size scaling methods[2,9,13,14)]. Here we skip all such technical details and focus on the phase diagrams that result (Fig. 4). In the case of absolutely neutral walls (Fig. 4a) the

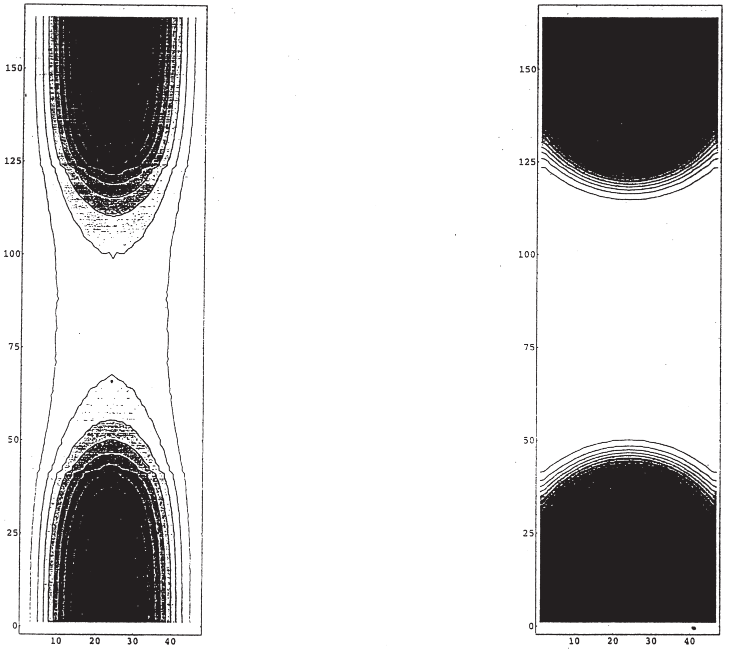


Fig. 2 (left part): Two-dimensional composition profiles for polymer mixtures with $N = 32$ in a $164 \times 48 \times 48$ geometry for a film with symmetric walls. B-rich regions are shaded darker. The walls attract the A component, $\varepsilon_w/k_BT = 0.16$. Case (a) refers to $\varepsilon = 0.02$ (above the wetting temperature) and average volume fraction of A-monomers $\bar{\phi} = 0.67751$, case (b) refers to $\varepsilon = 0.08$ (below the wetting temperature) and $\bar{\phi} = 0.5$. From Müller and Binder[2)]

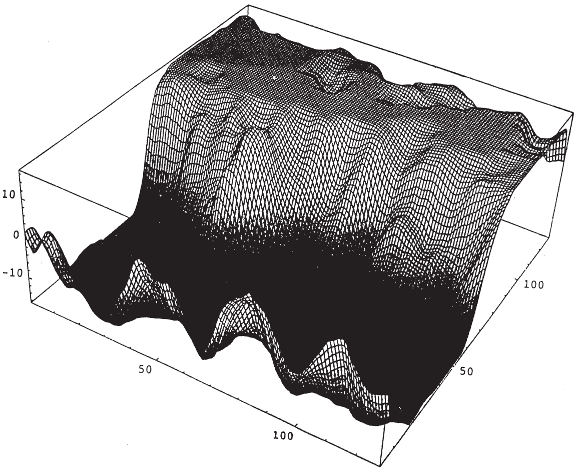
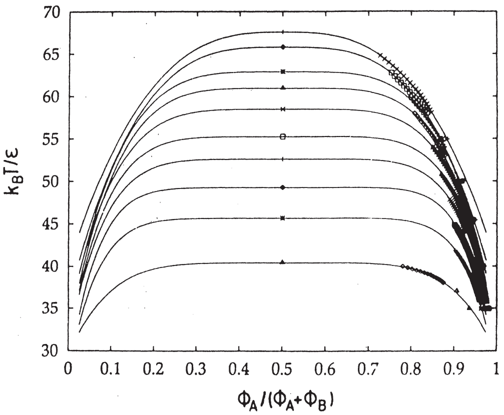


Fig. 3 (right part): Snapshot picutre of the coarse-grained interface position $z = h(x,y)$ between A-rich (above the interface) and B-rich regions (below the interface) in an antisymmetric film for a $128 \times 128 \times 32$ system with $N = 32$, $\varepsilon = 0.03$, and $\varepsilon_w/k_BT = 0$

critical composition $\overline{\phi}_{crit}(D)=1/2$ is independent of film thickness D. With decreasing D the critical temperature decreases from its bulk value ($T_{cb}=69.35$) and the shape of the coexistence curve gets flatter. This latter effect reflects the crossover from three-dimensional critical behavior to two-dimensional critical behavior[1]: remember that near $T_c(D)$ the coexistence curve is described by a power law, $\overline{\phi}^{(1,2)}_{coex} - \overline{\phi}_{crit}(D) \propto (1 - T/T_c(D))^{\beta}$, with an exponent β that „crosses over“[9] from its three-dimensional value ($\beta = 0.325$ for $D \to \infty$) to its two-dimensional value ($\beta = 1/8$). Also the compatibilization due to confinement can be described by power laws, namely $T_{cb}-T_c(D) \propto D^{-1/\nu}$ with $\nu = 0.63$ for $D \gtrsim D_{cross} \propto bN$ while $\nu = 1$ for[1,9,15] $D \lesssim D_{cross}$. Note that the compatibilizing effect of confinement (Fig. 4a) is much larger than predicted by a generalized Flory-Huggins theory[16], which also implies a mean-field (parabolic) shape of the coexistence curve for all D, since $\beta = ½$ independent of dimensionality in this approximation.



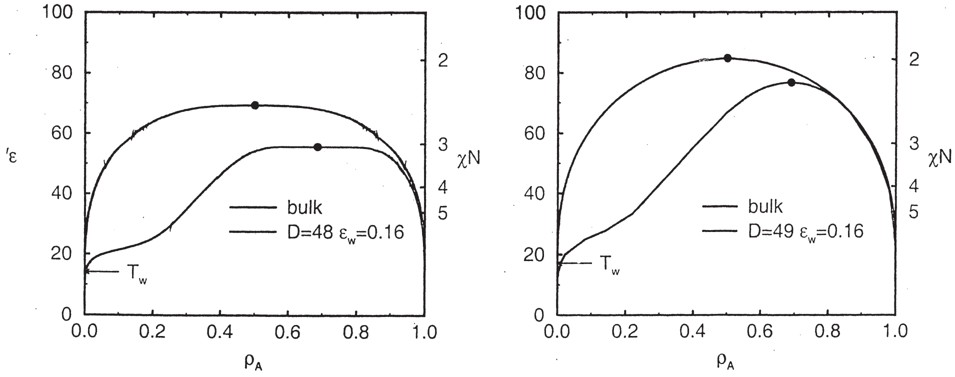


Fig. 4: a) Phase diagrams of the confined polymer mixtures for thin films of various thickness in the case of neutral walls, for N = 32 and D = 8, 10, 12, 14, 16, 20, 24, 28, 36 and 48 (from the bottom to the top). From Rouault et al.[9] b) Same as a) for D = 48 but for walls that both preferentially attract A ($\varepsilon_w = 0.16\ k_BT$). The corresponding (symmetrical) bulk phase diagrams are shown for comparison. The wetting transition temperature of a corresponding semi-infinite system is shown an arrow. c) Same as b) but result from a self-consistent field calculation. From Müller and Binder[2)]

„Capillary condensation“ of polymer blends confined by symmetric walls

By „capillary condensation“ one means that a gas condenses in a capillary already at a value of the chemical potenial which in the bulk still is in the one phase region. An analoguous phenomenon occurs for polymer blends between walls that preferentially attract one component: phase separation sets in at a value of $\Delta\mu$ (D) which is off phase coexistence in the bulk (remember $\Delta\mu = 0$ for a symmetrical mixture[1)]). This shift of the chemical potential $\Delta\mu_{crit}(D)$, at criticality also leads to a shift of $\bar{\phi}_{crit}(D)$ and the phase diagram no longer is symmetric (Fig. 4b). A particularly interesting phenomenon is the „bulge“ in the phase diagram near the temperature T_w of the (first order!) wetting transition (which has been located using Young's equation between the appropriate surface free energies that have been determined by special reweighting methods[2)]). This feature shows also up in a corresponding calculation based on the self-consistent field theory (Fig. 4c). The interpretation of this bulge is that this is a precursor of a triple point and a second critical point, which appear for small volume fraction φ_A of the A-rich phase at larger D. As $D \rightarrow \infty$, this critical point develops into the prewetting critical point and the triple point converges towards T_w.

While the self-consistent field theory gives rather good results for strongly segregated blends, it is not so good for weakly segregated blends since it overestimates the critical temperatures T_{cb}, $T_c(D)$ and again always implies $\beta = ½$, i.e. a simple parabolic shape of the coexistence curve near $T_c(D)$, as Flory Huggins theory does.

The interface localization transition in polymer blends confined between „antisymmetric“ walls

We now consider a blend where one wall attracts A while the other wall attracts B with the same stregth. When this wall energy ε_w is sufficiently strong, the interface that forms between the A-rich phase and the B-rich phase occurs (for $\overline{\phi}(D) = 1/2$) in the center of the film. However, for not so strong ε_w the interface gets bound to the walls (Fig. 3).

Thus in a simulation this localization transition can be probed very conveniently by varying ε_w at fixed temperature (Fig. 5). It is seen that for $\varepsilon = 0.03$, where bulk phases are almost completely segregated (Fig. 4a, b), in the localized phase ($\varepsilon_w \lesssim 0.07$) the order parameter is very close to its bulk value. In the thermodynamic limit $L \to \infty$, we hence expect macroscopic domains of A-rich phase, with $\rho_A \approx 0.98$ for $\varepsilon_w \lesssim 0.05$, separated from macroscopic domains of B-rich phases with $\rho_A \approx 0.02$ by walls running across the thin film. A study of the local order parameter $\phi_1 = \langle [\rho_B(z=1) + \rho_B(z=2)] \rangle / 2$ in the A-rich phase showns that $\phi_1 \lesssim 0.1$ for $\varepsilon_w \lesssim 0.05$ and even near the localicaztion transition ϕ_1 stays less than about 0.35: this implies that there is no well-defined region of B-rich phase at the surface of the A-rich domain at all, the interface is almost completely expelled from the A-rich domain, and an analoguous observation applies for the B-rich domain at the other wall.. It is important to recall that these results for the properties of the segregated phases in the limit $L \to \infty$ result from the semigrandcanonical ensemble, which yields results for the „pure phases“ separately, without any interfaces running across the film. In the canonical ensemble (Fig. 3), two interfaces running across the film must occur, and since these interfaces for $L = 128$ are not so far apart, the „wings“ of their profiles join in the interfaces bound to the wall and thus such simulations do not allow to get very precise data on the bulk properties of the segregated „pure phases“, due to such finite size effects. Similar finite size effects occur in the semi-grandcanonical simulation in the delocalized phase (Fig. 5): while for $L \to \infty$ the order parameter $\langle |2\rho_A - 1| \rangle = 0$, we get here a nonzero value of about 0.15 for $L = 128$; since for finite L there is a finite width of the distribution of the average position of the fluctuating interface on a scale L, and since our order parameter counts excursions of the interface both to the left and to the right as positive, this is a trivial finite size effect.

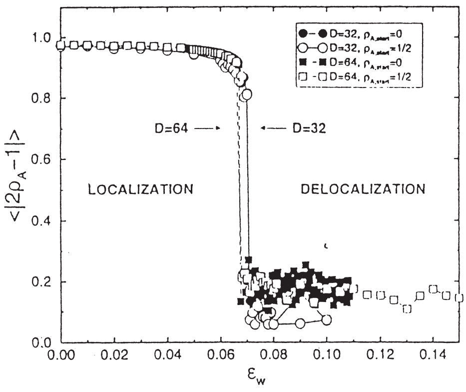


Fig. 5: Absolute value of the order parameter $\langle |2\rho_A = 1| \rangle$ plotted versus the wall interaction strength ε_w for the choice of parameters N = 32, $\varepsilon = 0.03$, L = 128, and two film thicknesses, D = 32 and D = 64. Using the grandcanonical ensemble, both starting configurations with volume fraction $\rho_A = 0$ and $\rho_A = 1/2$ were used.

If we would consider at fixed ε_w the variation of system properties with temperature, we expect at $T_c(D)$ close to T_w (Fig. 4) a first-order transition from the laterally inhomogeneous state (of the type of Fig. 3) to a laterally homogeneous state, with the fluctuating interface in the film center. A precise investigation of this transition still remains to be done.

Discussion

Confinement and forces due to walls have a pronounced effect on the phase diagram of polymer blends. In all cases studied, we find that the compability of the blend is enhanced (i.e., the critical temperature where lateral phase separation occurs is distinctly lower than the critical temperature of the bulk). But due to the gradual onset of surface enrichment layers, interfaces running parallel to the wall can form without a well-defined phase transition. The study of these phenomena is only at the very beginning - both asymmetries in chain lengths N_A, N_B and in chain stiffness need to be studied, long range surface forces$^{4)}$ and surface corrugation and/or roughness need to be included, etc. But we hope that this work will stimulate more experimental work to look into these questions.

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