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Different surface profiles in surface demixing of polymer blends

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The surface of the polymer mixture is simulated by Monte-Carlo method via condensing the polymer mixture against the solid wall and examining the free surface parallel with the wall. Depending on interactions present in the mixture and on the composition we find three representative situations of surface segregation effect in polymer mixtures described as *segregation in*, *segregation out*, and *surface double layer*. The segregation occurs across a realistic diffusive surface profile in contrast to theoretical approaches to this phenomenon working with a steplike density profile across the surface. Among the advantages of the present simulation, like the presence of compressibility of the studied system, there are also certain limitations, such as the lattice approximation.

INTRODUCTION

Surface composition of a compatible polymer blend can differ from that of the bulk blend due to a surface segregation effect. Many possible applications to surface and interface problems such as wetting, compatibility, friction of blends would arise from understanding and control of the surface demixing process. In fact, there is a high activity in this field towards measuring the surface profile or surface excess in polymer blends. Methods applied include forward recoil spectrometry (FRES),¹ called also elastic recoil detection (ERD),² secondary ion mass spectrometry (SIMS),³ or neutron reflection (NR).⁴ Though considerable progress has been made, there are still experimental problems like small depth resolution or inaccessibility of the shape of near surface depth profile where only integral excess over the profile is measured, or applications are made for model systems only. A combination of techniques mentioned above is highly recommended.^{4,5}

A theory^{6,7} of surface enrichment in polymer blends emerged somewhat earlier than the first experiments. Due to the complexity of the problem, the theory also has its limitation. The surface is modeled in the same way as the situation at the solid wall, thus the total density across the surface is a steplike discontinuous function. The surface energy is localized strictly to the surface, losing its close relation to the cohesion in the bulk and can be interpreted more through interactions across the surface. Changing the strict location of the surface energy with long-range surface interaction instead of short-range δ -function was used by Chen *et al.*⁸ This was done using the same model of the mixture at the wall where concentration at the wall is constant and does not fall to zero as it does at the real surface. Simulations on microscopic level together with a simulation algorithm allow here for a more realistic surface density profile.

In our Monte Carlo (MC) simulation here, the surface has a realistic continuous diffusive density profile; the surface demixing also occurs within this profile. The surface is formed by MC algorithm through cohesion between the chains in the bulk liquid phase and condensing this phase against the solid wall by adsorption. Moreover, the system

becomes compressible in contrast to the system studied by the theory.⁶⁻⁸ Except for advantages, however, we realize the limitations of our simulations, which are the lattice approximation and application to relatively short chains.

SIMULATION METHOD

In the MC simulations, we use an unique algorithm introduced by Madden.⁹ In contrast to simulations of bulk polymer melt with three-dimensional periodic boundary conditions, here the polymer chains are condensed towards a solid wall and periodic boundary conditions are used in two directions parallel to the wall. This condensation of polymer melt against the wall makes a regular interface with the vacuum, parallel with the wall, on the other side of the polymer slab and thus is ideally suited for studying surface phenomena. As was mentioned above the polymer slab becomes compressible because interactions in the slab balance its density through equilibrium between voids in the melt and vacuum above the condensed phase in contact. In the simulation we use cubic lattice with 50 sites in z direction and 22 in x and y directions. Periodic boundary conditions are used in x and y directions, with the solid wall placed at $z = 1$ and polymer chains (A and B) comprising 30 segments (monomers). Each chain is a self-avoiding walk with intra- and interchain volume exclusions. Each chain segment occupies one lattice site. One lattice spacing represents the size of one monomer which is (cca) 5–7 Å. Lattice nearest-neighbor interactions are imposed between segments and between the segments and the wall with energies $\epsilon_{AA}, \epsilon_{BB}, \epsilon_{AB}$, and $\epsilon_{AW}, \epsilon_{BW}$, respectively. Throughout this paper we will use reduced energies $e_{ij} = \epsilon_{ij}/kT$. For a segment at the wall to have a similar situation as the segment in the bulk, we use $e_{AW} = e_{AA}$ and $e_{BW} = e_{BB}$. Interaction energy of the segment with the void site is zero.

Different multichain configurations during the equilibration of each state are obtained by chain reptation, which is the most efficient method for sampling the configuration space in dense entangled medium. Random trial moves are evaluated by Metropolis criteria in their contribution to total

thermodynamic averages. Equilibration of each state starts from a well equilibrated athermal mixture with no interactions present and an initial sharp surface profile. After imposing interaction energy constraints and applying up to 3×10^8 trial reptations the equilibrium slab structure was obtained. From the three regions in the slab (situation at the wall, broad bulk region, and the surface of polymer melt) we are interested here only in the surface situation. In this computer experiment we evaluate the equilibrium total concentration profile of the mixture near to the surface as well as the profile of the components. A bulk composition c_B of the mixture in the text is the fraction of chains B from the total number of chains.

Further we analyze four typical situations we found depending on the parameters e_{ij} and blend composition. Generally we analyze miscible blend A/B with interactions satisfying $\chi < \chi_c = 2/(1 - \phi_v)N$, where $N = N_A = N_B$ is the polymerization degree and ϕ_v being volume fraction of voids in the mixture. Flory interaction parameter is given by classical relation $\chi = \Delta e_{AB}(Z - 2)/kT$, where $\Delta e_{AB} = e_{AB} - (e_{AA} + e_{BB})/2$ and Z is the coordination number of the lattice.

RESULTS AND DISCUSSION

(1) The first situation is trivial with no surface segregation for $e_{AA} = e_{BB} = e_{AB}$. It is instructive to note here that the mean cohesion energy in melt should be generally kept strongly negative, $e < -0.5$, in order to keep the condensed phase in these systems. For less strong cohesion, we occasionally obtained evaporated chains in these systems. From equation of state analysis of the bulk region of these systems, presented elsewhere,¹⁰ it is shown that the critical cohesion is $e_c = -0.311$.

(2) If one of the components A has smaller cohesion energy, e_{AA} , than the other two cohesions, e_{AB}, e_{BB} , in the system, then naturally this component has a lower surface free energy and fills the surface to minimize the total surface free energy of the system. This situation is shown in Fig. 1 for $e_{AA} = -0.5$, $e_{AB} = e_{BB} = -0.8$ for nearly symmetric composition $c_B = 0.465$ in volume fraction in bulk region. A large surface excess of A component can be recognized by the surface excess which it shows over the other component in the near surface region. In order to classify this situation in context with following situations, we denote this effect as *segregation out*. The composition dependence of this effect will be analyzed in context with the next situation (3).

(3) An interesting situation occurs for $e_{AA} = e_{BB} > e_{AB}$, representing the system with stronger heterocohesion than homocohesions. It seems that if both components have the same homocohesions, they should not segregate on the surface; moreover, a heterocohesion which is stronger than the homocohesions supports intermixing. This is especially true for symmetric composition as seen from Fig. 2. For asymmetric composition, on the other hand, the majority chains become a very good solvent for minority chains under the above conditions; thus, in order to expose the minority chains more to this favorable environment, these chains segregate from surface to the bulk, Figs. 2 and 3. Because of this

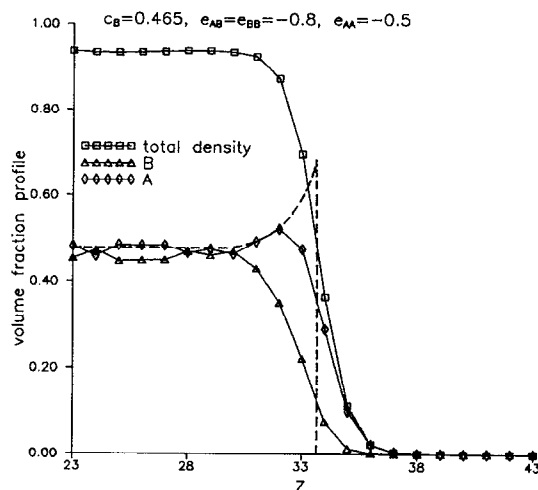


FIG. 1. Surface depth profiles in volume fraction of total mixture and both components versus the distance from the wall z for situation (2) with symmetric composition. Depicted is only the near surface region. Parameters shown by the insert. Schematic representation (---) of A component profile by Schmidt and Binder (Ref. 6).

characteristic we denote this as *segregation in*. We emphasize that the energetic effect here is interconnected with a geometric one since the minority chains expand under these good solvent conditions, as found in bulk studies,¹¹ and have thus larger difficulties in filling the narrow surface layer than the majority chains. Segregation from the surface coming from different coil sizes including only entropy effects was analyzed by Kumar *et al.*¹² From their studies it follows that purely entropic effect is small, leading to cca 1% surface excess only. On the other hand, including interactions affect the surface segregation dramatically.¹³

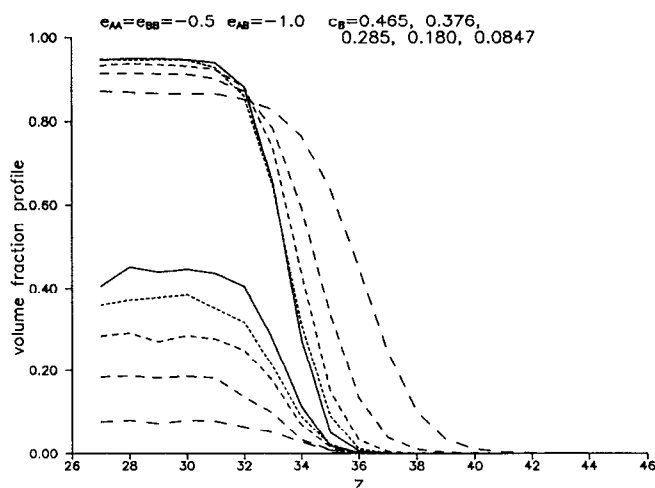
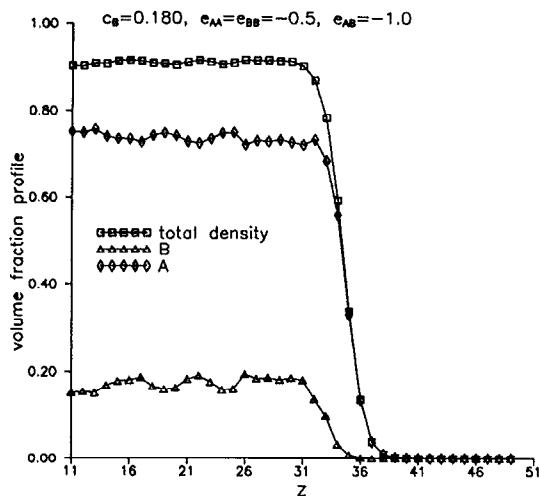


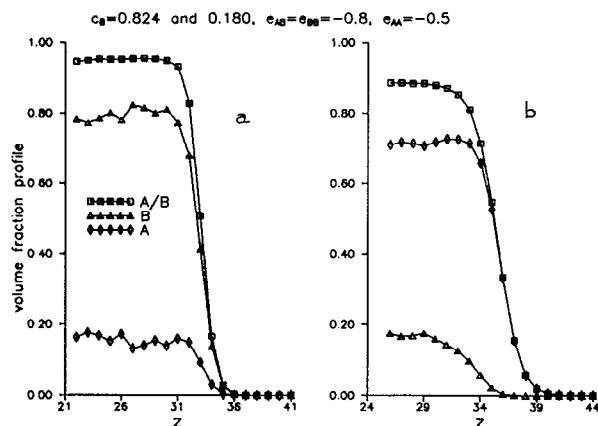
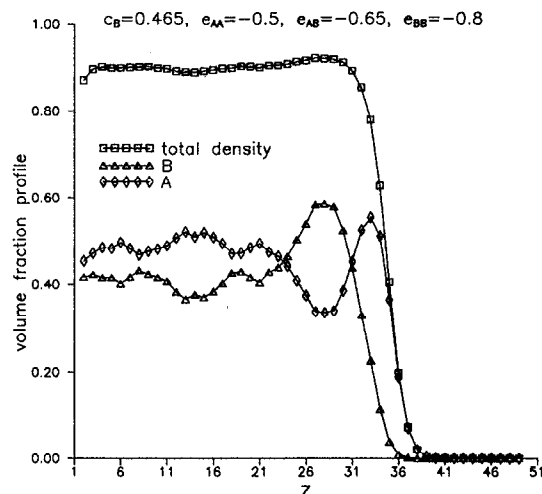
FIG. 2. Series of states in situation (3) showing continuous development of surface segregation when moving to composition asymmetry. The total mixture and component B volume fraction profiles are shown. The full line is valid for $c_B = 0.465$, lines with increasing dash size correspond to decreasing c_B .

FIG. 3. Profile of the mixture in situation (3) denoted as the *segregation in*.

After analyzing the situation (3) and its composition dependence, it is possible to analyze composition dependence in the previous case (2). Now it is obvious that in case (2) for $c_B \Rightarrow 1$, the *segregation in* of minority *A* chains coming from favorable heterocoheion and composition asymmetry can counteract the *segregation out* of *A* chains coming from the low e_{AA} cohesion. In accordance with this, Fig. 4(a) shows no segregation at $c_B = 0.842$ for parameters of situation (2). We see that these two forces are relatively well balanced in fact for the given set of parameters.

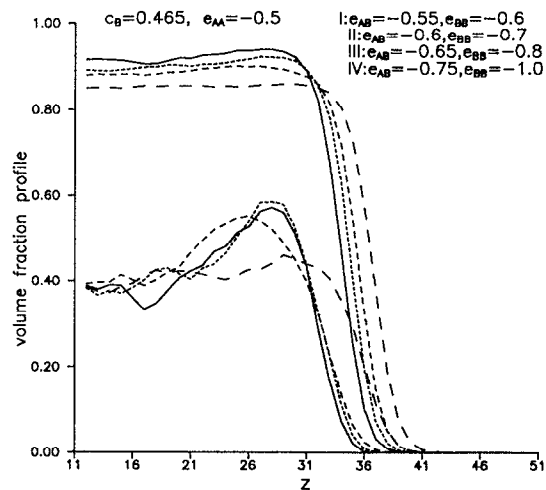
When moving towards $c_B \Rightarrow 0$, the *segregation out* of *A* chains (now majority) continuously disappears while *segregation in* of minority *B* chains appears as a result of asymmetric composition and favorable heterointeraction. In this case, however, both effects act in the same direction towards segregation, and thus as a result we see surface segregation on Fig. 4(b) for $c_B = 0.180$.

(4) If e_{AA} is different from e_{BB} and the cross interaction

FIG. 4. The composition dependence in situation (2) depicting profiles for two composition asymmetries at $c_B = 0.842$ (a) and $c_B = 0.180$ (b).FIG. 5. Situation (4) illustrated by depicting the *surface double layer* with *A* enriched outer layer and under the surface *B* enriched layer.

is located between homocoheions, this leads to another specific situation. The equilibrium profiles of a mixture with $e_{AA} = -0.5$, $e_{AB} = -0.65$, $e_{BB} = -0.8$ are depicted on Fig. 5 and a similar series of systems with continuously increasing difference in homocoheions on Fig. 6. Note that for all cases within this situation the classical Flory interaction parameter is $\chi = 0$ and nevertheless the surface segregation develops.

We have more effects acting concomitantly here: Component *A* with lower cohesion moves to the surface while that with stronger cohesion *B* segregates towards the bulk region both due to the effects explained in the above situations. However, the cross cohesion is not so strong as e_{BB} , and thus the excess of *B* expelled from the surface layer

FIG. 6. Series of states depicting continuous development of surface segregation in situation (4) for the same composition and varying interactions. Total mixture and component *B* profiles are shown. States I, II, III, IV correspond to curves (—), (---), (---), (—), respectively.

forms its own second layer below the surface excess of A , and does not spread into the bulk phase. This situation can be denoted as a *surface double layer*. If we move to $\chi < 0$ by keeping $e_{AA} \neq e_{BB}$ difference constant and increasing the cross interaction, then the peak of B dissolves in the bulk region and we move to situation (2).

Figures 2 and 6 illustrate also a finite compressibility of the simulated mixtures. The system here adjusts its density to cohesion energies e_{ij} , while in contrast it is still common in many MC simulations that the density of the system is preset and do not vary with interactions or temperature, thus the system being incompressible. For a series of states the total bulk volume fraction of the mixture depends on an average cohesion in the mixture. Accordingly, the surface profile is also less steep for lower densities.

A diverse behavior shown by the above analyzed situations manifests how rich a polymer blend surface behavior can be. Here we varied 4 parameters: e_{AA} , e_{BB} , e_{AB} , and the composition, and we do not preclude further structural details since we do not claim that we covered all the possibilities. In addition, if one considers further effects from glass transition or crystallization of components setting in, the situation may become even more variable.

Shapes of the profiles, Figs. 1 and 6, are very similar to those recently observed by Kramer *et al.*⁵ in their determination of concentration profile at the surface. One has to note that their profiles are influenced by depth resolution cca 100 Å and by a convolution of the real profile with the shape of resolution function, while we observed here the surface profiles directly.

In conclusion, it has been shown that different shapes of surface depth profiles can arise both as a result of interactions in the bulk and also from the combination of these interactions and the composition of the mixture. This is possible to show only if continuous physical connectivity of the surface with the bulk is allowed or the surface and the bulk are treated consistently, not separately. We hope that these intriguing different profiles will stimulate both experimental and theoretical research in surface demixing of polymer blends.

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