Entropic and Enthalpic Surface Segregation from Blends of Branched and Linear Polymers

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The surface segregation from blends of branched and linear polymers is investigated using Monte Carlo simulation. It is found that in the athermal system an entropic segregation is possible which favors the linear polymers at the surfaces. When an attraction between the polymer beads is introduced the branched polymers are found preferentially at the surface. The simulations provide a simple explanation of recent experimental observations on polyolefin materials in terms of enthalpic effects, but this suggests that the segregation behavior observed in experiments is not universal but should depend on details of fluid-fluid and fluid-surface interactions.

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The surface behavior of polymer melts and blends is of importance in several practical applications such as adhesion, lubrication, and polymer processing. In many cases, the properties of the material within a few angstroms of the surface are critical, e.g., when the surface finish of the processed polymer is of interest. In polymer blends a segregation of one of the components to the surface is possible even if the bulk blend is miscible and there is no preferential attraction between the surface and any of the polymer species. The design of polymeric materials will clearly benefit from an understanding of why this segregation occurs and how it might be controlled.

Recently there has been considerable attention focused on segregation caused by differences in the topology of the molecules of the polymer blend [1,2]. These experiments involve polyolefin materials where the elementary chemical units are similar (i.e., CH_x groups), but differences arise from the architecture of the molecules. An example is a blend of polyethylene (PE), which is a linear chain, and polyethylenepropylene (PEP), which has a single CH_3 side group hanging off every fourth backbone carbon atom. Every experiment on blends of polyolefins shows that the more branched component segregates to the surface, independent of the type of surface (air, silicon, etched silicon). In this paper I elucidate a possible mechanism for this segregation.

Sikka *et al.* [2] showed that the surface segregation from PE-PEP blends correlated with the statistical segment length of the molecules. They therefore suggested that the observed segregation was entropic in nature and argued that it was entropically favorable to place the chains with the *smaller* statistical segment lengths at the surface. A theoretical analysis of blends of stiff and flexible chains [3] concurred with the above argument. However, computer simulations clearly show the opposite effect [4], i.e., in a blend of stiff and flexible chains, the stiffer chains are always preferred at the surface. The analysis in terms of the flexibility is therefore questionable, and the real mechanism for the segregation is unknown.

In this paper I investigate via Monte Carlo simulations the surface segregation of blends of linear and branched polymers. The intermolecular potential is the sum of site-site hard-core plus attractive tail potentials. This model is chosen because it allows one to vary the attractive forces and, therefore, isolate the effects of entropy and enthalpy. When the fluid-fluid attractions are turned off and wall-fluid attractions (identical for both species) are present, the *linear* component segregates to the surface. The magnitude of this segregation increases as the strength of the wall-fluid attraction is increased. This may be attributed to the fact that the linear chains can pack against the surface more efficiently than the branched chains. Wall-fluid attractions provide an additional enthalpic incentive for the linear chains to segregate to the surface. However, when fluid-fluid attractions (of comparable strength to the wall-fluid attractions) are turned on, the *branched* polymers segregate to the surface. The reason for this is that the linear chains pack among each other more efficiently than the branched chains: In the presence of fluid-fluid attractions this provides an incentive for the linear chains to be in the bulk where their sites can have more neighbors than they can near a surface. This study suggests that the segregation observed in the experiments [1,2] is an entropy-mediated enthalpic effect caused by differences in packing. Since wall-fluid attractions favor the linear chains at the surface and fluid-fluid attractions favor the branched chains at the surface, the segregation is a strong function of the relative strengths of these attractions. This suggests that the behavior observed in experiments is not universal and rather different results might be obtained with more strongly interacting surfaces.

The molecules of both components consist of $N = 19$ tangent spheres; the molecules differ only in how these spheres are connected together as shown in Fig. 1. The site-site intermolecular potential $u_{ff}(r)$ is the same between any two beads in the system: $\beta u_{ff}(r) = \infty$ $(r < \sigma) = -\epsilon_{ff}[\sigma e^{-\kappa(r/\sigma-1)}/r - e^{-\kappa}/2]$ $(\sigma < r < 2\sigma) = 0$ $(r > 2\sigma)$, where κ is the inverse range of the shifted and cutoff Yukawa potential ($\kappa = 2.5$ in this work), σ
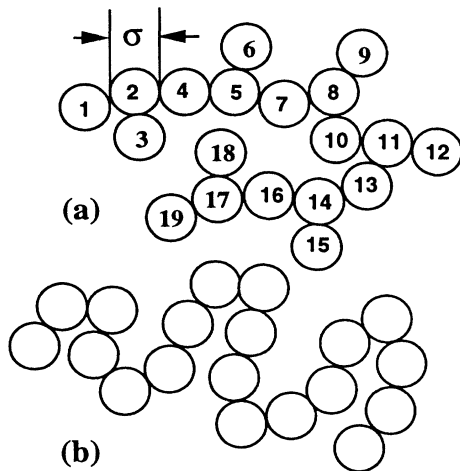

FIG. 1. Schematic representation of the (a) branched and (b) linear polymer molecules.

is the hard-core diameter, β^{-1} is Boltzmann's constant multiplied by the temperature, the subscript ff denotes "fluid-fluid," and ϵ_{ff} is the dimensionless strength of the attraction. The cutoff at $r = 2\sigma$ is employed because it results in an enormous savings in computer time when link cell lists are used to calculate the energy during the simulation. The range of the potential is chosen to mimic a Lennard-Jones potential. The fluid is confined between two identical and parallel walls. The wall-fluid potential is $u_{wf}(z) = \phi(z) + \phi(H - z)$, where H is the separation of the surfaces, z is the perpendicular distance from one of the surfaces, $\beta\phi(z) = \infty(z < 0) = -\epsilon_{wf}[e^{-\kappa z/\sigma} - e^{-\kappa}](0 < z < \sigma) = 0, (z > \sigma)$ and ϵ_{wf} is the dimensionless strength of the wall-fluid attraction. The form of the wall-fluid potential is obtained by considering the interactions to be the same as in the bulk fluid and integrating over the three-dimensional solid whose surface constitutes the wall. To estimate the proximity to the bulk phase transition point, I perform integral equation theory calculations which predict a bulk spinodal at a temperature corresponding to $\epsilon_{ff} \approx 1.09$. Note that the only difference between the molecules of the two species lies in the connectivity (or topology) of the molecules. The model, therefore, explicitly addresses the segregation due to solely topological differences.

Computer simulations are performed in the canonical ensemble with a parallelepiped simulation cell. The walls are placed in the z direction at a distance $H = 20\sigma$ apart, and periodic boundary conditions are employed in the other two directions. Two hundred molecules of each species (7600 beads in all) are used in these simulations and the period length L is adjusted so that the normalized average site density ρ ($\equiv NN_M\sigma^3/L^2H$, where N is the degree of polymerization and N_M is the number of molecules) is fixed at $\rho = 0.57$ which represents a liquidlike density. Values of ϵ_{ff} ranging

from 0 to 2 and ϵ_{wf} ranging from 0 to 3 are studied. The simulation algorithm is a generalization to branched-linear blends of techniques used successfully for linear chains [5]. Initial configurations are generated using a growth and equilibrium algorithm for off-lattice chains [6]. The system is then equilibrated until the average energy reaches a steady value and the density profiles are symmetric about the middle of the slitlike pore. Typically about 20 million attempted moves are required for equilibrium. The density profiles are then averaged over 80 to 100 million attempted moves. The mean square radius of gyration R_g^2 of the molecules is $\approx 4\sigma^2$ and $5\sigma^2$ for the branched and linear molecules, respectively.

Figure 2 depicts the total density of sites (both species included) as a function of the distance from the surface for four choices of wall-fluid and fluid-fluid attractions. In the athermal case ($\epsilon_{wf} = \epsilon_{ff} = 0$) there is an enhancement of sites at the surface relative to the bulk fluid, and the profile is oscillatory at short distances. These features are caused by the packing of the chains at the surface and are well understood [6]. When an attraction between the beads is introduced the molecules prefer the region away from the surface. This is because there is an energetic preference for the molecules to be among each other. In a bulk fluid, a given bead experiences an attraction from any other bead within a sphere of radius 2σ. If a bead is at the surface (say $z = 0$) then other sites are excluded by the surface from half of the volume (corresponding to $z < 0$), which decreases the total attraction experienced by the bead at the surface by roughly a factor of 2. Therefore there is an increase in the energy when a bead is taken from the bulk and placed near the surface, which makes the region near the surface energetically less favorable than the bulk region. As expected, an attractive wall-fluid potential causes an enhancement of chain density at the surface relative to the case where the wall-fluid interaction is athermal. This enhancement effect is
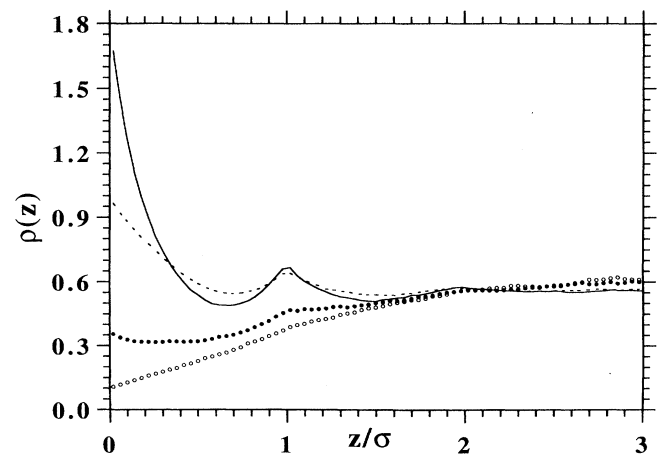

FIG. 2. Average density profile for $(\epsilon_{ff}, \epsilon_{wf}) = (0, 1)$ [—], (0,0) [- - -], (1,1) [●], and (1,0) [○].

stronger when the blend is athermal than when fluid-fluid attractions are present. When the wall-fluid and fluid-fluid attractions are of equal strength, the depletion mechanism due to the bulk attractions dominates. For these cases where wall-fluid and fluid-fluid attractions are of comparable strength, when attractions are present depletion effects dominate, and when attractions are absent, enhancement effects dominate. It transpires that the former favors segregation of branched molecules to the surface whereas the latter favors a segregation of linear molecules to the surface.

Figure 3 depicts the density profiles of linear and branched chains [denoted $\rho_i(z)$] relative to the "bulk" value in the middle of the pore (denoted ρ_b) for the athermal blend ($\epsilon_{ff} = 0$) and for hard walls ($\epsilon_{wf} = 0$) and attractive ($\epsilon_{wf} = 1$) walls (inset). The figure shows that in the purely entropic case ($\epsilon_{wf} = \epsilon_{ff} = 0$) the *linear* polymer segregates to the surface. The linear polymers are present in excess in the immediate vicinity of the surface even when wall-fluid attractions are present. At slightly larger separations ($1 < z/\sigma < 7$ in the inset of Fig. 3) a wall-fluid attraction favors presence of the branched molecules. When the blend is athermal, however, the observed segregation is quite small. When the strength of the wall-fluid attraction is increased the segregation of the linear polymers to the surface also increases (not shown).

A segregation of branched molecules to the surface occurs when fluid-fluid attractions are present. Figure 4 depicts the density profiles of branched and linear polymers relative to the bulk value for $\epsilon_{ff} = 1$ and $\epsilon_{wf} = 0$ and 1 (inset). In both cases the branched polymers are preferentially segregated to the surface. This is because it is energetically favorable to place the linear polymers *away* from the surface, since these molecules can pack against each other better than the branched molecules can. When
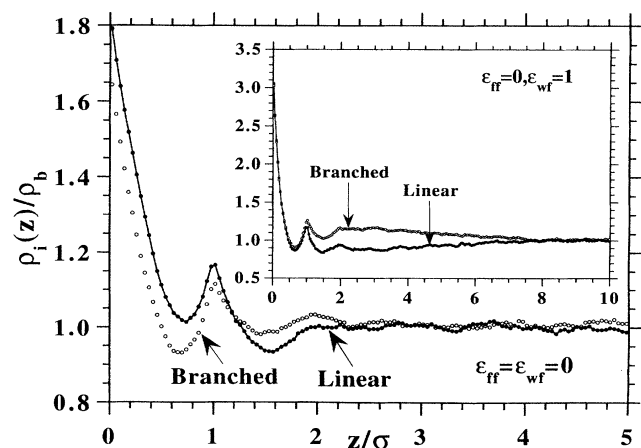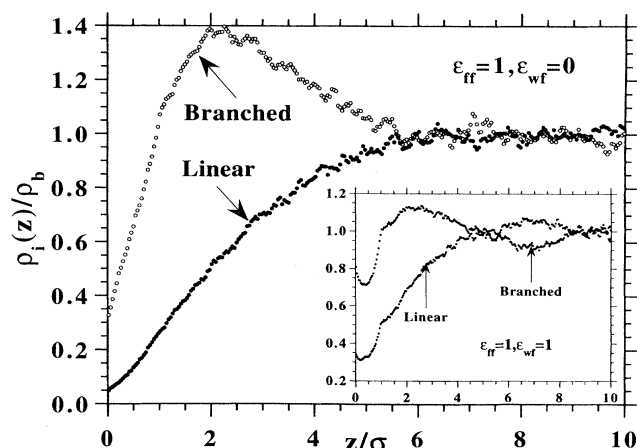

FIG. 4. Density profiles of branched and linear polymers in an attractive blend ($\epsilon_{ff} = 1$) normalized to the value in the middle of the pore for $\epsilon_{wf} = 0$ and 1 (inset).

wall-fluid attractions are introduced, segregation is somewhat moderated (see inset of Fig. 4). The dominant effect, however, is clearly due to the fluid-fluid attractive forces.

To quantify the bulk-fluid packing effects discussed above, simulations of the athermal bulk blend are performed. The average intermolecular site-site pair correlation functions obtained from these simulations are depicted in Fig. 5. It can be seen that the $g(r)$ between the linear chains is higher than that between the branched chains. Since the energy is proportional to $\int_0^\infty r^2 u_{ff}(r)g(r)\,dr$ (to first order in the inverse temperature), differences in packing caused by the topology of the molecules cause the branched molecules to be effectively more weakly interacting (lower cohesive energy) than the linear chains. The physical argument presented earlier is thus supported by Fig. 5. What is fascinating is that the

FIG. 3. Density profiles of branched and linear polymers in an athermal blend ($\epsilon_{ff} = 0$) normalized to the value in the middle of the pore for $\epsilon_{wf} = 0$ and 1 (inset).
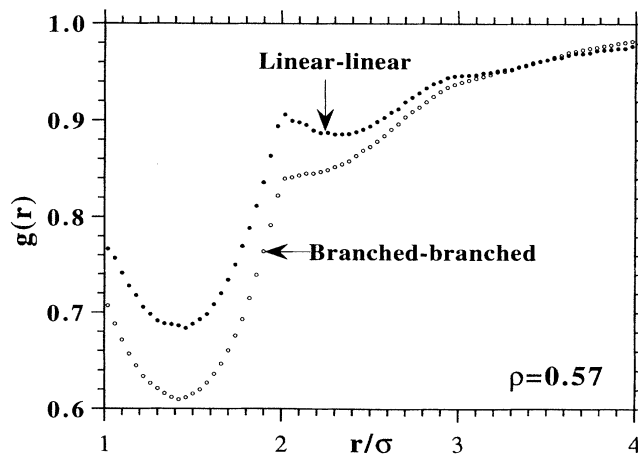

FIG. 5. Average site-site pair correlation functions $g(r)$ in an athermal bulk blend.

difference in the pair correlation functions is rather small, but apparently sufficient to cause the segregation at the surface seen in Fig. 4.

The results discussed so far have considered cases where the fluid-fluid and wall-fluid attractions were of comparable strength. If the wall-fluid attraction is stronger than the fluid-fluid attraction, then the chains pile up against the surface, and an enhancement of sites is seen near the surface. The total density profile is depicted in Fig. 6 for $\epsilon_{ff} = 1$ and $0 \leq \epsilon_{wf} \leq 3$. A transition from a depletion of sites near the surface (for $\epsilon_{wf} = 0$) to an enhancement of sites near the surface (for $\epsilon_{wf} = 3$) is seen. This transition is accompanied by a crossover in the segregation behavior, and for $\epsilon_{wf} = 3$ the linear chains are found in excess at the surface (see inset of Fig. 6). The physical mechanism for this is that the linear chains can pack against the wall more efficiently than the branched chains, and the presence of a wall-fluid attraction therefore favors the linear chains at the surface.

In conclusion, simulations are reported for blends of branched and linear polymers at surfaces. The segregation of one species to the surface is investigated both in the presence and in the absence of fluid-fluid and wall-fluid attractions. In the absence of fluid-fluid attractions, the *linear* polymers segregate to the surface. This segregation is very small, however, and probably not measurable in experiments. When fluid-fluid attractive forces are of comparable strength or stronger than the wall-fluid attractions, however, the *branched* polymers segregate to the surface as is also seen in experiments [1,2]. This segregation is caused by the fact that the linear
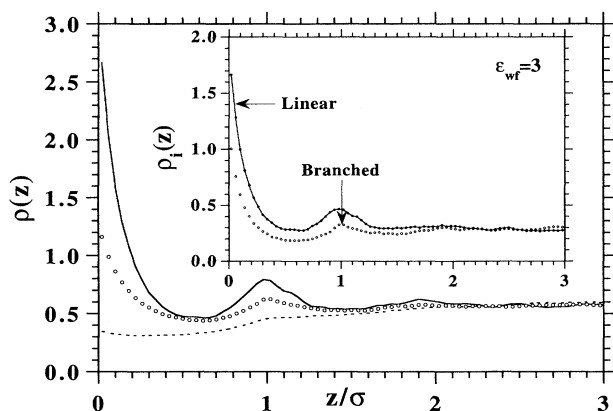
polymers can pack among each other more efficiently that the branched polymers and there is, therefore, an enthalpic advantage for them to be in the bulk where the coordination number is larger than near the surface. The segregation of the branched polymers is accompanied by a depletion of polymer beads at the surface. This is probably the case for a blend at a free (air) surface. This strongly suggests that the mechanism for the segregation seen in experiments is enthalpic in origin contrary to previous claims [2,3]. The results of this work predict that if the surface was more strongly interacting, then the experimentally observed behavior could be reversed. This work shows that even small differences in the topology of the molecules can result in substantial segregation of one of the species. These effects are expected to be magnified for longer chains and when the blend components differ in more significant ways, as is the case in real blends.

An important observation from this work, which has perhaps been overlooked earlier, is that the bulk fluid-fluid attractions can in some cases dominate the segregation from binary blends. Therefore if one desires to alter the surface properties of these materials it is important to study the bulk thermodynamics of the blends as well as to investigate the interactions of the individual species with the surface. This work also demonstrates that computer simulations of polymer molecules of complex architectures are feasible using straightforward extensions of methods used for linear chains. Simulations of chemically realistic polymer blends can be performed using these techniques and should be allowed for a quantitative comparison with experiment.

FIG. 6. Average density profile for $\epsilon_{ff} = 1$ and $\epsilon_{wf} = 0$ (- - -), 2 (O), and 3 (—). The inset shows the individual density profiles of the linear and branched components for $\epsilon_{ff} = 1$ and $\epsilon_{wf} = 3$.

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