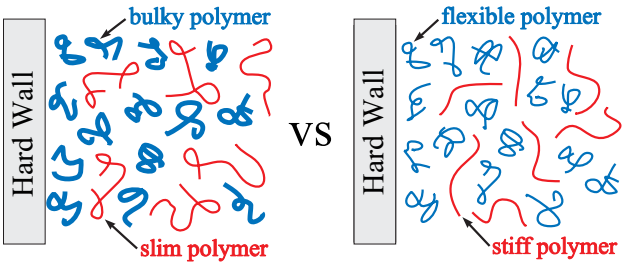
Entropic Surface Segregation from Athermal Polymer Blends of Slim and Bulky Polymers

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Abstract

Experiments, theory, and simulations have revealed an entropic preference at the surface of athermal blends for the component with the shorter statistical segment length. Here, we examined the resulting surface segregation for blends of slim and bulky polymers of equal molecular volume, using Monte Carlo simulations where the polymers are modeled as chains of impenetrable spheres. Comparing to analogous simulations for blends of stiff and flexible polymers [Spencer and Matsen, Macromolecules **2022**, *55*, 1120], we find that bulkiness has a considerably stronger effect on the surface segregation than stiffness, consistent with self-consistent field theory (SCFT) predictions for worm-like chains [Matsen, J. Chem. Phys. **2022**, *156*, 184901]. Furthermore, we demonstrate that, under special conditions, this mismatch in strength can lead to anomalous surface segregation of the component with the longer statistical segment length, as predicted by the SCFT.

Introduction

The surface properties of an alloy are largely dictated by the surface composition, which will inevitably differ from that of the bulk due to certain components having a stronger preference for the surface than others. In small-molecule systems, the surface preferences are generally enthalpic in origin. However, in polymeric alloys (i.e., blends), entropic considerations can also become important, particularly when the polymers are of high molecular weight and the enthalpic forces are reasonably balanced. It is known, for instance, that entropic preferences can result from disparities in the molecular volume of the polymers[1–5] and/or in the conformational size of the polymers.[6–17]

The effect of conformational asymmetry was first noticed by Sikka et al.[6,7] in experiments of polyolefin diblock copolymers, where the two blocks were chemically similar but with considerably different statistical segment lengths. The experiments observed that the diblock copolymers always ordered with the more compact (i.e., shorter segment length) component at the surface. Subsequent experiments by Scheffold et al.[8] on binary polyolefin blends found a similar surface preference for the polymer with the smaller average end-to-end length, R_0. Note that the comparison was for polymers of equal molecular volume, so as to isolate the effect of conformational asymmetry. Other experiments by Tretinnikov and Ohta[9,10] examined blends of isotactic and syndiotactic PMMA, where the monomers are identical but linked together differently resulting in a smaller R_0 for the syndiotactic polymer. Again, it was the more compact syndiotactic component that segregated to the surface.

It should be noted that there is some uncertainty whether the experiments were truly free of significant enthalpic effects. However, the experiments are supported by self-consistent field theory (SCFT) calculations of athermal blends,[11–13] which predict a positive surface excess

$$\phi_{\rm ex}(z) \equiv (\phi_2(z) - \bar{\phi}_2 - \phi_1(z) + \bar{\phi}_1)/2 \tag{1}$$

when $R_{0,1} > R_{0,2}$. Here, $\phi_\alpha(z)$ and $\bar{\phi}_\alpha$ are the volume fractions of component α at a distance

z from the surface and in the bulk, respectively, and $R_{0,\alpha}$ is the average end-to-end length of the α-type polymers in the bulk. Likewise, the behavior has also been confirmed by simulations.[14–16] As opposed to the experiments, we can be certain that the theory and simulations are completely free of enthalpic biases, and thus the resulting segregation can only be attributed to entropic effects.

Notably, the SCFT calculations by Wu et al.[12] predict that the excess adopts the form

$$\phi_{\mathrm{ex}}(z) = A_\rho F_\rho(Z) \tag{2}$$

for small degrees of conformational asymmetry, where the profile shape

$$F_\rho(Z) = \frac{(1+Z^2)}{\sqrt{\pi}} \exp(-Z^2) - \left(\frac{3Z}{2} + Z^3\right) \mathrm{erfc}(Z) \tag{3}$$

is expressed in terms of $Z = \sqrt{3/2}z/\bar{R}_0$, the distance from the surface scaled with respect to the average size of the polymers,

$$\bar{R}_0 \equiv \sqrt{(R_{0,1}^2 + R_{0,2}^2)/2} \tag{4}$$

Furthermore, the SCFT predicts that the amplitude of the excess scales as

$$A_\rho \propto \bar{\phi}_1 \bar{\phi}_2 \Delta R_0 \tag{5}$$

where $\Delta R_0 \equiv R_{0,1} - R_{0,2}$. However, this SCFT prediction is for the Gaussian-chain model, which does not discern between different types of conformational asymmetry.

The source of asymmetry in the two experimental systems is distinctly different. In the polyolefin system, the asymmetry originates primarily from a disparity in the bulkiness of side groups along the hydrocarbon backbone. For example, polyethylene (PE) is a long-slim polymer while polyethylethylene (PEE) is a relatively short-bulky polymer. Note that an

increase in bulkiness coincides with a reduction in contour length, given that the comparison is for polymers of equal molecular volume. In the case of the PMMA polymers, the conformational asymmetry arrises primarily due to a disparity in the stiffness of the polymers. Specifically, the isotactic PMMA is stiffer than the syndiotactic PMMA. Carignano and Szeifer[17] have, in fact, illustrated that entropic surface segregation is not solely dictated by ΔR_0, as implied by the SCFT of Gaussian chains. They did so by instead modeling diblock copolymers and polymer blends using semi-flexible polymers, where conformational asymmetry can result from a mismatch in flexibility (i.e., persistence length, ℓ_p) and/or a mismatch in bulkiness (i.e., contour length, ℓ_c).

Carignano and Szeifer examined their model using a relatively inefficient mean-field calculation, where only a small sample of the polymer conformations were considered. Concerned by the potential inaccuracy of their calculation, we reexamine the polymer blends using the SCFT for worm-like chains, where propagators or rather partial partition functions are used to enumerate all possible polymer conformations. Our study[13] focused on relatively flexible polymers (i.e., $\ell_p \ll \ell_c$), for which $R_0 \approx \sqrt{2\ell_p\ell_c}$. For small degrees of asymmetry, this implies that

$$\Delta R_0 = \frac{\bar{R}_0}{2}\left(\frac{\Delta\ell_c}{\bar{\ell}_c} + \frac{\Delta\ell_p}{\bar{\ell}_p}\right) \tag{6}$$

where $\Delta\ell_\beta \equiv \ell_{\beta,1} - \ell_{\beta,2}$ and $\bar{\ell}_\beta \equiv (\ell_{\beta,1} + \ell_{\beta,2})/2$ for $\beta = c$ and p. Although the excess, $\phi_{\rm ex}(z)$, continued to obey eq (2), the amplitude in eq (5) generalized to

$$A_\rho \propto \bar{\phi}_1\bar{\phi}_2\bar{R}_0\left(f_c\frac{\Delta\ell_c}{\bar{\ell}_c} + f_p\frac{\Delta\ell_p}{\bar{\ell}_p}\right) \tag{7}$$

where the coefficients, f_c and f_p, are functions of $\bar{\ell}_p$. Consistent with eq (5), $f_c = f_p$ in the Gaussian-chain limit of $\bar{\ell}_p = 0$. However, apart from this limit, the coefficients satisfy the inequality $f_c > f_p$, implying that disparities in bulkiness, $\Delta\ell_c$, produce stronger surface segregation than disparities in stiffness, $\Delta\ell_p$. Furthermore, as result of this mismatch in f_c and f_p, anomalous surface segregation of the less compact polymer can occur under special

conditions. In particular, the polymer must be bulkier with a sufficient stiffness so as to produce a larger R_0 but not so much so as to reverse the segregation.

Monte Carlo (MC) simulations by Yethiraj, Kumar, and coworkers have also examined these two sources of entropic segregation. Their first set of simulations studied a series of stiff+flexible blends involved linear polymers with equal polymerizations of N = 10, 25, 50, 100, and 500, where half the polymers were flexible and half were semi-flexible.[18,19] The second set of simulations examined slim+bulky blends involving polymers of N = 19, where half were perfectly linear like PE and half possessed small side groups like PEE.[20] Although both sets were performed with the same hard-sphere chain model, the authors did not report sufficient information regarding the degree of conformational asymmetry to allow for quantitative comparisons. Furthermore, it is questionable whether the polymerization of the slim+bulky blends was sufficient to represent true polymeric behavior. In any case, there is a far more serious issue. It has recently been shown that the simulations for the stiff+flexible blends were quantitatively and, in fact, qualitatively inaccurate, even for the shortest $N = 10$ polymers, as a result of insufficient equilibration and statistics.[14] Although there are now accurate predictions for the stiff+flexible blends,[14] the previous simulations[20] for slim+bulky blends may also need to be corrected. Not only were they limited to a similarly small number of MC steps, the problem would have been exacerbated by the fact that the inclusion of side groups inevitably slows down the MC dynamics.

Here, we perform alternative MC simulations for the slim+bulky blends that can be compared on an equal footing with the revised simulations for the stiff+flexible blends.[14] To avoid the slower dynamics resulting from the explicit inclusion of side groups, we create the mismatch in bulkiness by a simpler means. This time, both polymer species are modeled as linear chains of hard spheres, but with different sized monomers. We also examine blends where the bulky polymers composed of the larger monomers are assigned a small bending penalty in an attempt to reproduce the anomalous surface segregation predicted by SCFT.[13]

Simulations

We employ a generalization of the model used by Yethiraj, Kumar, and coworkers,[18,19] where the polymers are represented by tangentially-connected chains of impenetrable spheres, as illustrated in Figure 1. The position of the ith monomer of the jth polymer is denoted by the vector $\mathbf{r}_i^{(j)}$. The first n_1 polymers are composed of N_1 small monomers of diameter $\sigma_1 \leq 1$, and the remaining n_2 polymers are composed of N_2 large monomers of diameter $\sigma_2 = 1$. Hence, the diameter of the larger monomers defines our length scale. In some of the simulations, we apply a bending penalty, $\kappa_\alpha k_B T \cos(\theta)$, to the bonds of the α-type polymers, where κ_α is a dimensionless bending modulus and θ is the bending angle defined in Figure 1. The polymers are placed in a simulation box of size $L_x \times L_y \times L_z$ with impenetrable walls in the z-direction and periodic boundaries in the x- and y-directions.

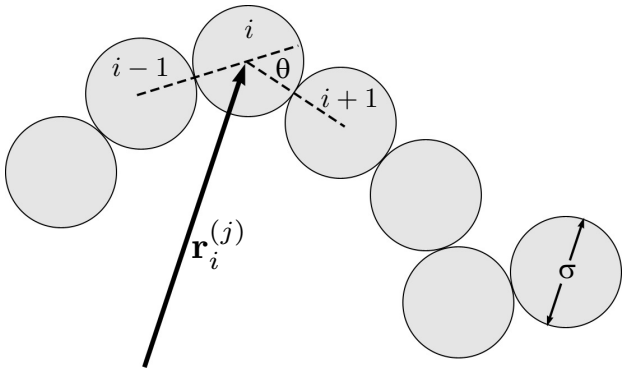


Figure 1: Illustration showing a portion of the jth polymer. The vector $\mathbf{r}_i^{(j)}$ denotes the position of the ith monomer, θ is a bond angle, σ is the diameter of the monomers.

The model is simulated in the canonical ensemble, using the Metropolis Monte Carlo algorithm described in ref 14. Our trial moves include reptation where a chain moves along its contour, crankshaft where a middle monomer (i.e., $1 < i < N_\alpha$) rotates about the axis connecting its bonded neighbors, and an end-rotation move where an end monomer (i.e., $i = 1$ or N_α) rotates about its bonded neighbor. The average acceptance rates for the parameters of our simulations are generally about 30%, 5%, and 10%, respectively. The previous swap move, where the positions of $\alpha = 1$ and 2 polymers are interchanged, is

dropped since it requires $N_1 = N_2$ and $\sigma_1 = \sigma_2$.

Given that the monomers are hard spheres, we are able to specify the average volume fraction of each component as a function of z. For the slim polymers, the volume fraction is given by the convolution

$$\phi_1(z) = \int \rho_1(z - Z) H(\sigma_1/2 - |\mathbf{R}|) d\mathbf{R} \tag{8}$$

of the Heaviside function, $H(x)$, and the density of monomer centers

$$\rho_1(z) = \frac{1}{L_y L_z} \left\langle \sum_{j=1}^{n_1} \sum_{i=1}^{N_1} \delta(z - z_i^{(j)}) \right\rangle \tag{9}$$

Here, Z and $z_i^{(j)}$ are the z-components of $\mathbf{R}$ and $\mathbf{r}_i^{(j)}$, respectively, and the angle brackets denote ensemble averages. The volume fraction for the bulky polymers, $\phi_2(z)$, is given by analogous expressions. To quantify the conformational asymmetry defined by

$$\gamma \equiv \frac{R_{0,1}}{R_{0,2}} - 1 \tag{10}$$

we also evaluate the end-to-end lengths of the polymers

$$R_{0,\alpha} = \left(\left\langle |\mathbf{r}_{N_\alpha}^{(j)} - \mathbf{r}_1^{(j)}|^2 \right\rangle \right)^{1/2} \tag{11}$$

where the ensemble average is over all polymers of type α for which the middle monomer occupies the bulk region (i.e., $0.4L_z < z_i^{(j)} < 0.6L_z$ for $i = N_\alpha/2$).

To initialize the system, the polymers are assigned *random-walk* configurations in a small $10 \times 10 \times 32$ simulation box. The overlaps between monomers rapidly disappear and the polymers quickly adopt equilibrium distributions of the end-to-end vectors as the system relaxes. The concentrations, $\phi_\alpha(z)$, are slower to equilibrate, partly because there is no swap move. Therefore, we equilibrate for a prolonged duration of around 10^{12} MC steps. To ensure

there are no significant finite-size effects, we then periodically repeat the system in the x- and y-directions producing a $20 \times 20 \times 32$ simulation box and then we equilibrate again for a further 10^{12} MC steps. Once this is completed, we collect statistics over roughly 10^{13} MC steps. Note that these levels of equilibration and statistics are about 10^5 times greater than those used by Yethiraj.[20] To assess the accuracy of our results, we divide the statistics into a number of equally-sized intervals. Based on the statistical variation between the samples and reflections about the center of the box, we conclude that our concentrations, $\phi_\alpha(z)$, are accurate to approximately the line widths of our plots. The statistically inaccuracies in $R_{0,\alpha}$ are exceptionally small, less than 0.01%.

Results

We begin by considering blends of flexible polymers (i.e., $\kappa_\alpha = 0$), where the conformational asymmetry is created by varying their relative bulkiness. The polymerization of the bulky polymers is fixed at $N_2 = 40$ and the diameter of their monomers is set to $\sigma_2 = 1$, resulting in a short contour (i.e., fully-extended) length of $\ell_{c,2} = N_2\sigma_2 = 40$. The bulky polymers are then blended with a series of slim polymers with $N_1 > 40$ monomers. Once N_1 is chosen, the diameter of the monomers is dictated by our requirement of equal molecular volumes,

$$\sigma_1 = \sigma_2(N_2/N_1)^{1/3} = (40/N_1)^{1/3} < 1 \tag{12}$$

invoked so as to avoid entropic segregation due to a volume disparity.[1–5] It thus follows that the ratio of the contour lengths is

$$\frac{\ell_{c,1}}{\ell_{c,2}} = \frac{N_1\sigma_1}{N_2\sigma_2} = \left(\frac{N_1}{40}\right)^{2/3} > 1 \tag{13}$$

To match the polymer density of the previous simulations for stiff+flexible blends,[14] we fill the $20 \times 20 \times 32$ simulation box with $n_1 = n_2 = 96$ polymers of each type; the 50-50 blend

composition tends to maximize the amplitude of the segregation (see eq (5)).

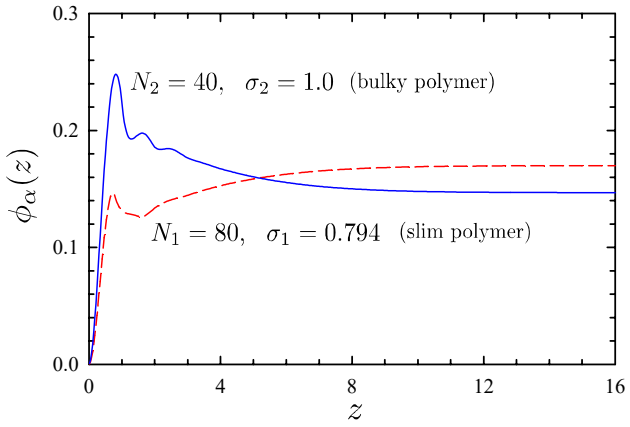


Figure 2: Concentration of slim polymers, $\phi_1(z)$, with $N_1 = 80$ monomers of diameter $\sigma_1 = 2^{-1/3}$ (solid curve) and bulky polymers, $\phi_2(z)$, with $N_2 = 40$ monomers of diameter $\sigma_2 = 1$ (dashed curve). Both polymers are flexible (i.e., $\kappa_\alpha = 0$).

Figure 2 shows concentration profiles, $\phi_1(z)$ and $\phi_2(z)$, for a blend of slim and bulky polymers of polymerizations $N_1 = 80$ and $N_2 = 40$, respectively. Even though the conformational asymmetry between the polymers is merely $\gamma = 0.18$, there is nevertheless a considerable preference for the bulky polymers at the surface. (Note that $0.2 \lesssim \gamma \lesssim 0.6$ for the polyolefin blends of Sikka et al.[6]) The profiles exhibit oscillations next to the wall due to the tendency of monomers to pack in successive layers.[14,18,19] However, the ordering rapidly vanishes as the distance from the wall increases, and the profiles then decay smoothly to the bulk compositions. As opposed to real systems, the bulk does not dwarf the surface region, and consequently the surface segregation perturbs the bulk concentrations away from 50-50 composition. We could, in principle, tweak n_1 and n_2 to restore a 50-50 bulk composition, although the fact that n_1 and n_2 must remain integers limits how accurately this can be done. In any case, past simulations have shown that such deviations from 50-50 composition have a negligible effect on the excess.[14] Indeed, the SCFT prediction in eq (5) implies that the surface segregation in Figure 2 for the bulk concentrations of $\bar{\phi}_1 = 0.170$ and $\bar{\phi}_2 = 0.147$ should only deviate 0.5% from that of equal bulk concentrations. Hence, we can consider the resulting surface excess to be equivalent to that of a 50-50 blend with bulk concentrations

of $\bar{\phi}_0 = (\bar{\phi}_1 + \bar{\phi}_2)/2 = 0.159$.

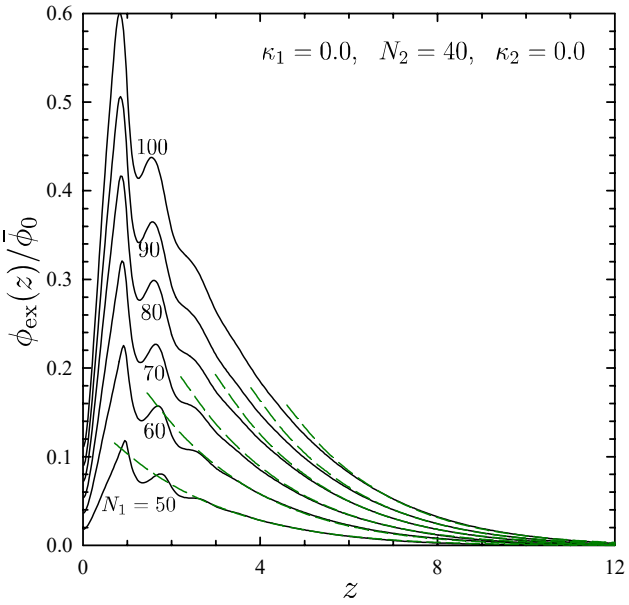


Figure 3: Excess concentration, $\phi_{ex}(z)$, of bulky polymers of polymerization $N_2 = 40$ in blends containing slimmer polymers of larger polymerizations N_1. The dashed curves are fits to $\phi_{ex}(z) = A_\rho F_\rho(Z)$ at large z.

Figure 3 compares the surface excess, $\phi_{ex}(z)$, from the simulation in Figure 2 with those of other simulations for different ratios of N_1 and N_2. Naturally, the amplitude of the excess increases as the conformational asymmetry increases. The dashed curves show fits of the long-range part of the excess to eq (2). Table 1 lists the fitting parameters, A_ρ, and the average end-to-end lengths of the polymers, $R_{0,\alpha}$, used to evaluate $\bar{R}_0$ and γ. As expected and also observed previously,[14,16] the universal profile, $F_\rho(Z)$, agrees most accurately at the smaller degrees of conformational asymmetry.

Figure 4 plots the amplitude of the long-range excess as a function of conformational asymmetry. The increase in A_ρ is found to be approximately linear in γ, consistent with the SCFT predictions.[12,13] The plot includes a curve for the stiff+flexible blends from ref 14, the results of which are also included in Table 1. For equivalent values of γ, the surface segregation is markedly stronger for the slim+bulky blends, as previously predicted by the SCFT calculations for worm-like chains.[13]

As pointed out in ref 13, the fact that an asymmetry in bulkiness affects A_ρ more so

Table 1: Average end-to-end lengths of the polymers and amplitudes of the surface excess.

N_1	κ_1	$R_{0,1}$	N_2	κ_2	$R_{0,2}$	A_ρ
50	0.0	8.93	40	0.0	8.45	0.043
60	0.0	9.29	40	0.0	8.42	0.085
70	0.0	9.61	40	0.0	8.39	0.125
80	0.0	9.89	40	0.0	8.36	0.172
90	0.0	10.13	40	0.0	8.34	0.218
100	0.0	10.35	40	0.0	8.31	0.270
40	0.5	8.96	40	0.0	8.50	0.022
40	1.0	9.61	40	0.0	8.51	0.046
40	1.5	10.45	40	0.0	8.53	0.071
40	2.0	11.44	40	0.0	8.55	0.099
50	0.0	8.94	40	0.5	8.92	0.022
50	0.0	8.95	40	0.7	9.16	0.011
50	0.0	8.96	40	1.0	9.58	-0.003
50	0.0	9.98	40	1.5	10.43	-0.030

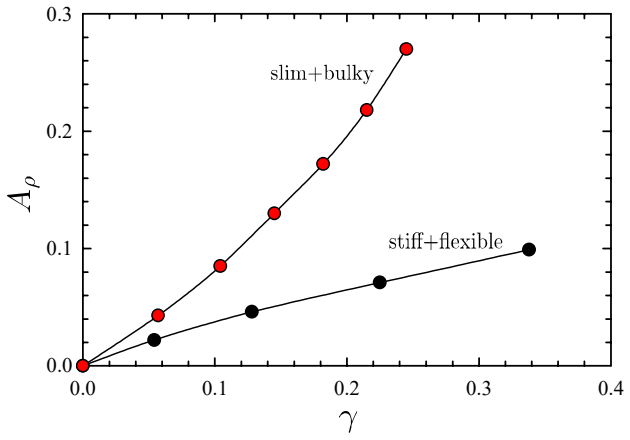


Figure 4: Amplitude of the long-range surface excess, A_ρ, plotted as a function of conformational asymmetry, γ, for the slim+bulky blends in Figure 3 and the stiff+flexible blends from ref 14.

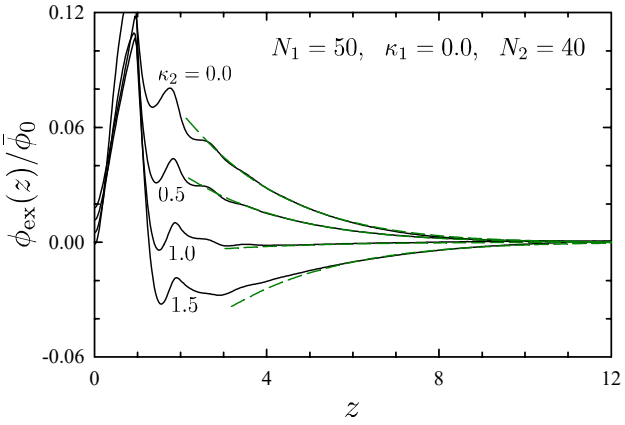


Figure 5: Analogous plots to those of Figure 3, but for blends of slim flexible polymers, $N_1 = 50$ and $\kappa_1 = 0$, with bulky polymers, $N_2 = 40$, of various stiffness, $\kappa_2 \geq 0$.

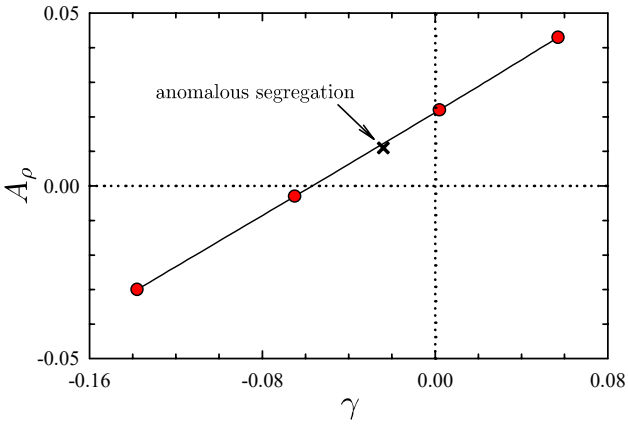


Figure 6: Analogous plot to that of Figure 4, but for the blends in Figure 5. The cross denotes an additional blend corresponding to $\kappa_2 = 0.7$, for which the surface segregation is anomalous.

than an asymmetry in stiffness sets up the possibility for anomalous segregation, where A_ρ is opposite in sign to γ. To test this possibility, we add a bending energy to the bulky polymers of our blend with $N_1 = 50$ and $N_2 = 40$. We choose the blend with the smallest degree of conformational asymmetry partly because it conforms most accurately with eq (2) but also because of the high computational cost of simulating stiff polymers. The bending modulus, κ_2, of the bulky polymers is increased in increments of 0.5 until there is a clear reversal in the excess. The resulting excesses are plotted in Figure 5 along with fits to eq (2). The values of A_ρ and $R_{0,\alpha}$ are again tabulated in Table 1. Based on the dependence of A_ρ on γ plotted in Figure 6, we expect anomalous segregation over the interval $0.5 \lesssim \kappa_2 \lesssim 0.9$, which is, in fact, straddled by our increments of $\Delta\kappa_2 = 0.5$. Therefore, we perform one final simulation for $\kappa_2 = 0.7$, the results of which are also listed in Table 1 and denoted by a cross in Figure 6. As anticipated, the values of $A_\rho = 0.011$ and $\gamma = -0.024$ are opposite in sign, confirming that the surface segregation is indeed anomalous.

Discussion

The present simulations for slim+bulky blends have been intentionally designed to match the previous simulations for stiff+flexible blends,[14] so as to ensure that the quantitative comparison in Figure 4 is unbiased. In particular, we made certain to use the same basic model for both systems. Furthermore, all simulations were performed with identical simulation boxes and equal polymer concentrations. Both sets of blends also involved the same compact polymer with $N_2 = 40$, $\sigma_2 = 1$, and $\kappa_2 = 0$. The only potential issue was that the conformational size of the $\alpha = 2$ reference polymer varied among the different blends, but this proved to be negligible. Indeed, as evident from Table 1, the variation remained within a narrow interval of $8.31 \leq R_{0,2} \leq 8.55$. This is consistent with previous simulations[14] that found the conformational size of a polymer to be relatively insensitive to the other polymers in the melt.

It should be noted that Figure 4 does not represent a direct comparison of the coefficients, f_c and f_p, in eq (7). While the polymers of the flexible+stiff blends have identical contour lengths (i.e., $\Delta\ell_c = 0$), the polymers of the slim+bulky blends do not have identical persistence lengths (i.e., $\Delta\ell_p \neq 0$). In the latter case where $\kappa_1 = \kappa_2 = 0$, the persistence lengths should be proportional to the monomer diameters, since this length scale is all that distinguishes the two polymers. Note, we are again assuming that the blend conditions have little effect on the conformational size of the polymers. Therefore, we expect the ratio of persistence lengths in the slim+bulky blends to be

$$\frac{\ell_{p,1}}{\ell_{p,2}} \approx \frac{\sigma_1}{\sigma_2} = \left(\frac{40}{N_1}\right)^{1/3} < 1 \tag{14}$$

Thus, the bulky polymers ($\alpha = 2$) will be somewhat stiffer than the slim polymers ($\alpha = 1$), and therefore the segregation of the slim+bulky blends depends on both f_c and f_p. We could have removed the dependence on f_p by increasing κ_1 of the slim polymers until $\Delta\ell_p = 0$, but we our aim was simply to show that bulkiness has a stronger effect than stiffness. This point can be illustrated by just rewriting eq (7) as

$$A_\rho \propto \bar{\phi}_1\bar{\phi}_2\bar{R}_0\left((f_c - f_p)\frac{\Delta\ell_c}{\bar{\ell}_c} + 2f_p\frac{\Delta R_0}{\bar{R}_0}\right) \tag{15}$$

where eq (6) is used to remove the explicit dependence on $\Delta\ell_p/\bar{\ell}_p$. Given that the comparison in Figure 4 is for identical values of $\Delta R_0/\bar{R}_0$, it immediately follows that $f_c > f_p$ as predicted by the SCFT. Although eq (15) was derived for small degrees of conformational asymmetry, the logic also extends to large asymmetries.

Notably, our study adds to mounting evidence that entropic segregation due to conformational asymmetry is reasonably consistent among different systems. In particular, the general preference for compact polymers is now supported by numerous experiments,[6–10] theoretical calculations,[11–13] and simulations,[14–16] and the evidence to the contrary has been largely dismissed.[14] On top of that, our simulations suggest that the enhanced effect of bulkiness

relative to that of stiffness as originally predicted by SCFT[13] is also generally true, given how different the simulations are from the SCFT calculations. Not only do they employ different models, the SCFT calculations were for polymer/air surfaces while the current simulations corresponded to polymer/solid surfaces.

Although the agreement between different systems is, in general, just qualitative, the long-range part of the excess quantitatively matches the profile shape, $F_\rho(Z)$, in eq (3). In fact, there is now overwhelming evidence that $F_\rho(Z)$ is universal for small degrees of conformational asymmetry. The derivation of $F_\rho(Z)$ was based on the SCFT of Gaussian chains,[12] but it nevertheless agrees precisely with the SCFT for worm-like chains, provided that the polymer contours are much longer than their persistent lengths (i.e., $\ell_c \gg \ell_p$).[13] Furthermore, the profile matches the excesses in lattice simulations of stiff+flexible blends,[16] off-lattice simulations of stiff+flexible blends,[14] and now off-lattice simulations of slim+bulky blends. We note that an analogous universality has been predicted for entropic segregation due to disparities in molecular volume,[2,3] and likewise confirmed by simulations.[4]

In reality, the universality of $F_\rho(Z)$ should be of no surprise. The derivation[12] involves splicing together a short-range profile near the surface with the $F_\rho(Z)$ for the long-range part of the profile. The outer solution is dictated by how the perturbation of the surface relaxes to the bulk, and only relies on the assumption that the polymers obey Gaussian statistics, which is universally true for polymer melts of high molecular weight. As such, $F_\rho(Z)$ is merely the one-dimensional inverse Fourier transform of the Debye function for ideal Gaussian chains.[12]

Although the outer profile is universal, the inner solution depends on the details of the system. As a consequence, the amplitude of the outer profile, A_ρ, cannot possibly be universal. Indeed, this was illustrated in ref 16, where simulations were performed with difference surface fields. In real systems such as polyolefins,[6–8] the bulkiness of the polymers typically results from the addition of side groups. Thus, the details of the side groups, such as their size and spacing, can potentially affect the amplitude of the segregation. It is likely

that these effects will be small for polymer/air surfaces, but this may not be the case for polymer/solid surfaces. The layering that occurs next to solid surfaces due to molecular packing will be sensitive to the detailed structure of the side groups, and thus this could, in turn, have an appreciable impact on the amplitude, A_ρ, of the long-range excess.

As mentioned in the Introduction, Yethiraj[20] has performed simulations for slim+bulky blends in which the side groups of the bulky polymers (e.g., the C_2H_5 groups of polyethylethelene) were explicitly included. In that case, the side groups were modeled as spheres attached to every second monomer along the backbone. However, we doubt the validity of their results given that we required approximately 10^5 times more MC steps to achieve accurate results. It is also suspicious that some of their excesses extend similar distances from the wall to those in Figure 3, even though their molecules are much shorter. Furthermore, their concentration profiles are not generally consistent with $F_\rho(Z)$. Perhaps, this could be because their molecules are more representative of oligomers than polymers. If so, then their results may not actually be relevant to high-molecular-weight polymers. In any case, it would be interesting to investigate the sensitivity of entropic surface segregation to the finer details of bulkiness.

Summary

Using Monte Carlo simulations, we examined surface segregation from athermal blends involving polymers with identical molecular volumes but different end-to-end lengths, $R_{0,\alpha}$ ($\alpha = 1$ and 2). The polymers were modeled as a sequence of N_α hard spheres of diameter σ_α with a dimensionless bending modulus of κ_α. The first part of our study considered slim+bulky blends, where the conformational asymmetry resulted from a mismatch in contour length. These simulations considered flexible polymers (i.e., $\kappa_1 = \kappa_2 = 0$) with different contour lengths (i.e., $N_1\sigma_1 > N_2\sigma_2 = 40$). The bulky $\alpha = 2$ polymers with the shorter contour length were found to segregate to the surface. Provided the conformational asymmetry,

γ, was not too large, the long-range part of the excess, $\phi_{\rm ex}(z)$, conformed to eq (2) with the universal profile, $F_\rho(Z)$, and an amplitude, A_ρ, that increased more or less linearly with γ, as predicted by SCFT.[12,13]

The molecular volumes and polymer densities were chosen to match previous simulations of the same model, where the conformational asymmetry resulted from a mismatch in persistence length.[16] Those simulations considered stiff+flexible blends where the polymers had equal contour lengths (i.e., $N_1\sigma_1 = N_2\sigma_2 = 40$) but different bending moduli (i.e., $\kappa_1 > 0$ and $\kappa_2 = 0$). In that case, the flexible $\alpha = 2$ polymers segregated to the surface. Again, the long-range part of $\phi_{\rm ex}(z)$ exhibited the universal profile with an amplitude that increased linearly for small γ.

In both types of blends, the more compact polymer (i.e., $\alpha = 2$) with the smaller end-to-end length, $R_{0,2}$, generally segregated to the surface. However, the segregation was considerably stronger in the slim+bulky blends (see Figure 4), which is consistent with SCFT predictions for worm-like chains.[13] The SCFT calculations illustrated how this mismatch between the effects of bulkiness and stiffness could lead to anomalous segregation, where the comformationally-larger polymers segregate to the surface. The last part of our study confirmed this by imparting the bulky polymers with an appropriate stiffness (see Figure 6). After years of contradictory results (see the discussion in ref 14), a consistent picture appears to be emerging for the phenomena of entropic segregation due to conformational asymmetry.

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