On the Control of Surface Enrichment in Polymer Blends and Copolymers

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ABSTRACT: We discuss a model for the equilibrium behavior of flexible polymer blends and copolymers near surfaces and focus on how the *bulk* properties of such melts affect their surface properties. Using a self-consistent field theory, derived previously from density functional theory, we obtain a general expression for the segregation in a structurally and interaction potential asymmetric blend near a flat, neutral surface. For an *athermal* structurally asymmetric blend, we predict no segregation—as is consistent with recent simulations. However, for a blend of typical polyolefins, we predict that the segregation is controlled by differences in the pure-component "beta" parameters, $\beta = R_g(\rho_{mol})^{1/2}$, where R_g is the radius of gyration and ρ_{mol} is the number density of chains. This result is consistent with both previous theoretical work and with experiments on polyolefin diblock copolymers. Lastly, we show how nearly all of these results can be understood from the perspective of a simple pure-component scaling theory.

I. Introduction

Polymer blends have received considerable attention commercially as materials whose properties may be tailored much in the same manner as metal alloys. The surface properties of polymeric materials are important in numerous applications, for example as adhesives, coatings, and lubricants. Hence, one issue of practical interest is how to control the surface segregation of one component of a polymer blend relative to another. Given a particular substrate, the structure of a polymer melt near a surface is determined by a number of factors including surface roughness or morphology, interactions between the surface and the melt, and the bulk properties of the melt.

While all of these elements are important, in this paper we focus on the interplay and competition between the bulk polymer properties of conformational entropy, packing effects, and cohesive energy in controlling surface segregation. To focus on the influence of bulk effects (as opposed to specific surface interactions and surface packing), we consider segregation of a structurally asymmetric flexible blend of linear polymers at a flat, neutral surface. As we shall argue, our coarse-grained analysis for this case is most directly applicable to free (air or vacuum) surfaces. While the same mechanisms for surface enrichment are possible at a solid surface, under certain conditions, other surface-specific effects, such as surface packing (which might, for example, vary as a function of surface roughness), can then also come into play.[1] In any case, once the relation between bulk and surface properties are known, one can then control—to a degree at least—the behavior of a blend near a particular surface by playing off bulk properties against surface-specific interactions.

There has been some controversy surrounding the role of these bulk effects in determining surface segregation. The role of conformational (or, equivalently, "structural") asymmetry was first considered by Fredrickson and Donley[2] within a density functional theory.[3] Their analysis yielded the general prediction that the surface segregation of a blend should be controlled by the difference in the "beta" parameters of the two components; the smaller β component being enriched at the surface. The beta parameter is defined by $\beta^2 = R_g{}^2\rho_{mol}$, where R_g and ρ_{mol} are the radius of gyration and number density of chains in each of the bulk pure-component melts, respectively. However, their analysis relied upon a perturbative expansion of a singular surface field that led to erroneous scaling of the amplitude of segregation. A more careful analysis by Wu *et al.*[4] using the self-consistent field (SCF) theory of Helfand and Tagami[5] revealed the importance of the compressibility in controlling the degree of segregation and gave the correct scaling of the amplitude of surface segregation. They also showed that, because of chain screening, the influence of the surface on chain conformations extends only over a microscopic length ξ (typically ∼10 Å at melt densities for flexible polymers) from the surface. The prediction for the direction of segregation was found to be in accord with experiments performed by the Bates group on polyolefin diblock copolymers showing surface preference of the block with the lower β parameter, i.e., the more "flexible" block.[6] Numerical evaluation of the self-consistent field equations for both blends[8] and copolymers[9] gives results consistent with the analytical theory and experiments. This prediction seems also to be in agreement with recent experiments of Scheffold *et al.*[7] on random copolymer blends—for the polymer−*air* surface; for the polymer−*solid* surface, no detectable enrichment of either species is seen. On the other hand, simulations by Yethiraj, Kumar, Hariharan, and Schweizer[10] performed on chains of about N = 10−100 hard-sphere monomers showed the stiffer chain (as determined by a bending potential between adjacent monomers in the simulations) only slightly enriched at the surface. These results were in accord with calculations using a surface version of the polymer reference interaction site model (polymer-RISM or PRISM) on the

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same system.[10] Recent work by Kumar *et al.* has extended these simulations to chains up to 500 monomers in length with similar results.[1] However, in subsequent simulations by Yethiraj,[11] attractive interactions were introduced between chain monomers, and it was found that the more flexible chains were again found at the surface.

Using the liquid-state density functional theory of Chandler, McCoy, and Singer (CMS),[12] we have since been able to derive a more general version of polymer SCF theory.[13] In the Gaussian thread limit, we find that our present theory corresponds to the previous SCF theory of Helfand and Tagami (HT),[5] but without the usual assumption of symmetry in the interactions in the bulk. We show herein that by removing this approximation, our present theory yields predictions for the athermal blend that are consistent with the simulations. Furthermore, we present arguments for including the effect of bulk attractive interactions on the surface segregation, which not only explain the subsequent simulations by Yethiraj but also suggest that the symmetric model of HT is appropriate for polyolefin blends with similar compressibilities.

The remainder of this work is organized as follows. In section II, we review the basic ideas of the polymer field theory that we will apply to polymer blends. In section III, we consider the general case of an arbitrary blend of linear thread polymers. We derive an expression that predicts the sign of the surface segregation given the blend composition, structure of the molecules, and their interactions in the bulk. Section IV treats an athermal blend of such molecules, finding no preferred segregation, consistent with recent simulations. However, in section V, we include attractive interactions within the bulk and find that for the most common polyolefins the segregation is controlled by the Helfand−Sapse β parameters of each component. This leads to the prediction that the component with the smaller β, i.e. the more "flexible" component, is enriched at a neutral surface, in agreement with recent experiments and our previous work. In section VI, we show that almost all the results of sections III, IV, and V can be explained in terms of a recent pure component theory. Last, in section VII, we summarize our results and discuss the relation between the present work and other experiments and theories.

II. Field Theory for Polymers in the Thread Limit

Our model system consists of a binary homopolymer blend of linear chains of type A and type B in a volume V at temperature T. Each chain of type K (K = A, B) has N_K identical sites with an average site number density $\bar{\rho}_K$ and radius of gyration R_K (measured in the pure-component melt). Let $\mathbf{r}_{\alpha i K}$ denote the position of the αth site on the ith molecule of type K. Finally, all energies are scaled in units of k_BT, where k_B is Boltzmann's constant.

To address the issue of surface segregation, we will compute the density profile for each component near a neutral surface. For simplicity we perform our calculations for the case of a hard, flat surface, since our theory, based on a coarse-grained thread description, is insensitive to short-ranged details of the shape of the surface potential. Since the surviving feature at this level of description is a depletion region near the surface, our theory corresponds most directly to either a free surface, or to a solid surface where there exists a depletion region (as will be the case when bulk attractive interactions dominate over attraction to the surface).

Let $\rho_K(\mathbf{r})$ be the density of sites of type K at point $\mathbf{r}$ in an external field $v_w(\mathbf{r})$ that describes the surface. Specifically, we define

$$\rho_K(\mathbf{r}) = \sum_{\alpha} \rho_{\alpha K}(\mathbf{r}) \tag{1}$$

where

$$\rho_{\alpha K}(\mathbf{r}) = \langle N_{cK}\delta(\mathbf{r}-\mathbf{r}_{\alpha 1K})\rangle \tag{2}$$

is the density of sites α of chains of type K at point $\mathbf{r}$, $N_{cK} \equiv \bar{\rho}_K V/N_K$ is the total number of chains of type K, and $\delta(\mathbf{r})$ is the Dirac "delta" function. The brackets $\langle ... \rangle$ denote an equilibrium average over the positions of all sites on all chains in the liquid.

Donley *et al.*[14] and Sen *et al.*[15] have made use of the molecular density functional theory of Chandler, McCoy, and Singer (CMS)[12] to reduce this many chain average to an average over the conformations of a single chain in an effective field $w_K(\mathbf{r})$:

$$\rho_{\alpha K}(\mathbf{r}) \approx \langle N_{cK}\delta(\mathbf{r}-\mathbf{r}_{\alpha 1K}) \exp[-\sum_{\eta=1}^{N_K} w_K(\mathbf{r}_{\eta 1K})]\rangle_0 \tag{3}$$

where

$$w_K(\mathbf{r}) = v_{wK}(\mathbf{r}) + u_{mK}(\mathbf{r}) + w_{0K} \tag{4}$$

and $v_{wK}(\mathbf{r})$ is an external potential that acts on a site of type K. The constant w_{0K} ensures that the average density of sites of type K remain $\bar{\rho}_K$. For the case we will consider in this paper of a hard wall occupying the $x-y$ plane, the external potential has the form

$$v_w(\mathbf{r}) = v_w(z) = \begin{cases} \infty, & z < 0, \\ 0, & z > 0, \end{cases} \tag{5}$$

and is felt identically by all sites, i.e., $v_{wK}(\mathbf{r}) = v_w(\mathbf{r})$ for all K. With this form for $v_w(\mathbf{r})$, the density profiles depend only upon the coordinate z, i.e. $\rho_K(\mathbf{r}) = \rho_K(z)$. The hard potential yields the boundary condition $\rho_K(0) = 0$. Furthermore, as our liquid is semi-infinite and we expect the density to reach its bulk value at a finite distance from the wall, we set $w_{0K} = 0$.

The function $u_{mK}(\mathbf{r})$ above is a medium induced potential that mimics the effects of the other chains in the liquid on a single type-K site. In our CMS-type theory it is obtained by an expansion of the free energy about an ideal reference state that has the same density profiles $\rho_K(\mathbf{r})$ as the true system. We define the deviation of the total density of sites of type K from its average bulk value as $\Delta\rho_K(\mathbf{r}) = \rho_K(\mathbf{r}) - \bar{\rho}_K$. Then, to first order in an expansion in terms of $\Delta\rho_K(\mathbf{r})$, the medium-induced potential has the form[13]

$$u_{mK}(\mathbf{r}) = -\sum_{K'} \int d\mathbf{r}'\, c_{KK'}(\mathbf{r}-\mathbf{r}')\, \Delta\rho_{K'}(\mathbf{r}') \tag{6}$$

where $c_{KK'}(\mathbf{r})$ is the direct correlation function between sites of type K and K′ a distance $r = |\mathbf{r}|$ apart in the bulk and can be thought of as a screened interaction potential. An approximate expression for $c_{KK'}(\mathbf{r})$ is available from the polymer reference interaction site model (polymer-RISM or PRISM) equation for a blend,[16] which we will discuss further below.

Finally, the brackets $\langle ... \rangle$ in eq 3 denote an average with the statistical weight $P_K\{\mathbf{r}\}$, which is the *bulk* probability density for a type-K chain to be in a configuration $\{\mathbf{r}\} \equiv \{\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N_K}\}$. Information on the chain architecture and thus conformational entropy are contained in $P_K\{\mathbf{r}\}$. By specifying the form of $P_K\{\mathbf{r}\}$, the above liquid-state theory allows us to model polymer architecture in as much detail or as crudely as is needed.

The model of the polymer structure that we use herein is the so-called "Gaussian thread" model (or limit).[13,17] While sacrificing some quantitative accuracy, this coarse-grained description may enable us to identify more easily any trends that exist. For this model, the chain of discrete sites α is replaced by a continuum of sites denoted by the contour variable *s*, i.e. $\mathbf{r}_\alpha \rightarrow \mathbf{r}(s)$. The intramolecular probability density $P_K[\mathbf{r}(s)]$ models the chains as beads connected by springs and takes the familiar Gaussian form[20,21]

$$P_K[\mathbf{r}(s)] \sim \exp\left[-\frac{3}{2b_K^{\,2}}\int_0^{N_K} ds \left(\frac{d\mathbf{r}(s)}{ds}\right)^2\right] \qquad (7)$$

with b_K being the statistical segment length of a type-K chain. It is chosen such that the size $R_K = (N_K b_K^2/6)^{1/2}$ of our model chain is the same as our original. Making use of eq 7, eqs 1 and 3 in the continuum site limit become

$$\rho_K(\mathbf{r}) = \frac{\bar{\rho}_K}{N_K}\int_0^{N_K} ds\; q_K(\mathbf{r},s)\; q_K(\mathbf{r},N_K - s) \qquad (8)$$

where the function $q_K(\mathbf{r},s)$ obeys the equation

$$\frac{\partial q_K(\mathbf{r},s)}{\partial s} = \frac{b_K^{\,2}}{6}\nabla^2 q_K(\mathbf{r},s) - w_K(\mathbf{r})\; q_K(\mathbf{r},s) \qquad (9)$$

with the "initial" condition $q_K(\mathbf{r},0) = 1$.

The thread limit is then taken by shrinking the hard-core site diameters to zero but retaining the compressibility of the original system in an approximate way.[13] For the systems we will consider, the site potentials are expected not to be very long-ranged; hence, we make the thread approximation

$$c_{KK'}(\mathbf{r}) \rightarrow \hat{c}_{KK'}(0)\; \delta(\mathbf{r}), \qquad (10)$$

i.e., replace the direct correlation function $c_{KK'}(\mathbf{r})$ by a delta function with equivalent integrated strength $\hat{c}_{KK'}(0) = \int d\mathbf{r}\; c_{KK'}(\mathbf{r})$. In making this approximation, we are essentially ignoring density variations over the range of the intermolecular potentials, and are incorporating (in a coarse-grained manner) packing effects arising from *individual* monomers into the amplitudes $\hat{c}_{KK'}$. To what degree this local packing information is retained in the thread theory depends upon how the direct correlation amplitudes are determined. We will discuss this approximation in more detail in the following sections.

Within the PRISM theory,[18] the three independent $\hat{c}_{KK'}(0)$ can be related to the partial structure factors at zero wavevector, $\hat{S}_{KK'}(0)$. These factors can, in turn, be related to the bulk osmotic susceptibilities of each component and the bulk compressibility. Hence, one can obtain the $\hat{c}_{KK'}(0)$ either from theory (given a choice for the closure relation to be used in the PRISM equations), as we shall do in the section considering athermal blends, or from experiment, as in the section addressing polyolefin blends.

III. General Treatment of Polymer Blends

In this section we derive a general expression that predicts the sign of surface enrichment for a polymer blend with arbitrary structural and interaction potential asymmetry.

Any atomistic model for a blend of short-branched polymers, when coarse-grained to a Gaussian thread (as described in the previous section), will be characterized by a matrix of $\hat{c}_{KK'}$ amplitudes, statistical segment lengths b_K, monomer densities $\bar{\rho}_K$, and polymerization indices N_K. However, in this continuum limit, one has the freedom to rescale what one means by the definition of a monomer. For instance, rescaling the monomer index of type-B polymers by a factor λ results in the rescaled quantities (denoted by a prime)

$$\begin{aligned} s' &= \lambda s \\ N'_B &= \lambda N_B \\ b'_B &= b_B/\sqrt{\lambda} \\ \bar{\rho}'_B &= \lambda \bar{\rho}_B \\ \hat{c}'_{AB}(0) &= \hat{c}_{AB}(0)/\lambda \\ \hat{c}'_{BB}(0) &= \hat{c}_{BB}(0)/\lambda^2 \end{aligned} \qquad (11)$$

By choosing the rescaling parameter to be

$$\lambda = \sqrt{\hat{c}_{BB}(0)/\hat{c}_{AA}(0)} \qquad (12)$$

we can set $\hat{c}_{AA}(0) = \hat{c}'_{BB}(0)$, although we now have rescaled values for other parameters as well. Equation 9 then becomes

$$\begin{aligned} \frac{\partial q_A(\mathbf{r},s)}{\partial s} &= \frac{b_A^{\,2}}{6}\nabla^2 q_A(\mathbf{r},s) - w'_A(\mathbf{r})\; q_A(\mathbf{r},s) \\ \frac{\partial q_B(\mathbf{r},s')}{\partial s'} &= \frac{(b'_B)^2}{6}\nabla^2 q_B(\mathbf{r},s') - w'_B(\mathbf{r})\; q_B(\mathbf{r},s') \end{aligned} \qquad (13)$$

where the rescaled fields can now be written in the symmetric form

$$\begin{aligned} w'_A(\mathbf{r}) &= \chi'\frac{\Delta\rho'_B(\mathbf{r})}{\bar{\rho}'_0} + \zeta'\frac{\Delta\rho_A(\mathbf{r}) + \Delta\rho'_B(\mathbf{r})}{\bar{\rho}'_0} \\ w'_B(\mathbf{r}) &= \chi'\frac{\Delta\rho_A(\mathbf{r})}{\bar{\rho}'_0} + \zeta'\frac{\Delta\rho_A(\mathbf{r}) + \Delta\rho'_B(\mathbf{r})}{\bar{\rho}'_0} \end{aligned} \qquad (14)$$

in terms of only two (positive) quantities (in place of the three $\hat{c}_{KK'}(0)$): $\chi' = (\bar{\rho}'_0/2)(\hat{c}_{AA}(0) + \hat{c}_{BB}(0) - 2\hat{c}'_{AB}(0))$ (one definition of the Flory "χ" parameter[5,16]) and $\zeta' = -(\bar{\rho}'_0/2)(\hat{c}_{AA}(0) + \hat{c}'_{BB}(0))$ (a rescaled bulk modulus), with $\bar{\rho}'_0 = \bar{\rho}_A + \bar{\rho}'_B$.

The above rescaled equations, (13) and (14), are essentially Helfand–Tagami SCF theory.[5] The equivalence in this limit allows us to extend the perturbative analysis of Wu *et al.*[4,30] to the general case of nonzero "χ" (details are given in the Appendix). We find as a result that the sign of the surface enrichment is controlled by the expression

$$(\epsilon' - 1) + \left(\frac{\bar{\rho}_A - \bar{\rho}'_B}{\bar{\rho}'_0}\right)\frac{\chi'}{\zeta'} \qquad (15)$$

where $\epsilon' \equiv (b_A/b'_B)^2$ is a conformational asymmetry parameter. (Only the first term in (15) was identified for the $\chi = 0$ case considered in ref 4.) The sign of the segregation is defined such that component *B* is preferred at the surface when the above expression is positive. The corresponding rescaling-invariant expression governing surface segregation is (recall that we expect $\hat{c}_{KK'}(0) < 0$)

$$\left[\frac{b_A^{\,2}}{b_B^{\,2}}\sqrt{\frac{\hat{c}_{AA}(0)}{\hat{c}_{BB}(0)}} - 1\right] + \left[\frac{\bar{\rho}_A\sqrt{-\hat{c}_{AA}(0)} - \bar{\rho}_B\sqrt{-\hat{c}_{BB}(0)}}{\bar{\rho}_A\sqrt{-\hat{c}_{AA}(0)} + \bar{\rho}_B\sqrt{-\hat{c}_{BB}(0)}}\right]\left[\frac{-\hat{c}_{AB}(0)}{\sqrt{\hat{c}_{AA}(0)\hat{c}_{BB}(0)}} - 1\right] \qquad (16)$$

From this analysis, we see that a positive χ' produces a favorable interaction of the minority component (lower $\bar{\rho}$) with the wall. This is because the potential due to Flory χ interactions felt by the minority component is stronger—as it is proportional to the density of the majority component. Near the wall, the *total* monomer density is depleted out to a healing length set by ζ'. The minority component monomers are thus attracted to the wall region so that unfavorable contacts with the majority species can be minimized. In the absence of Flory χ interactions, this attraction mechanism is inoperative.[4] We note that in our previous paper,[4] we guessed that the effect of nonzero χ might be simply to enhance the amplitude of segregation, regardless of its "sign". While this effect does occur, it is in fact a higher, second-order, correction, while the effect described above by (16) is first-order in the quantity $\bar{\rho}_A(-\hat{c}_{AA}(0))^{1/2} - \bar{\rho}_B(-\hat{c}_{BB}(0))^{1/2}$.

Note that in the above expressions, it is the *mixed-state* $\hat{c}_{KK'}(0)$ that enter. Hence the above rule does not directly make predictions from the *pure-component* bulk properties. However, for athermal blends and polyolefin blends we are able to construct reasonable approximations to these mixed state amplitudes. Thus, eq 16 will be used to examine both of these cases in the following sections.

IV. Athermal Blends

Here we examine the behavior of an athermal blend near a neutral surface. By athermal we mean that the sites of the molecules only interact *via* hard core potentials; hence, there is no temperature dependence. The effect of adding attractive interactions will be treated in the following section. The athermal blend serves only as an (artificial) model system since attractive interactions must exist in all real polymers, being the source for cohesion of the melt. Nonetheless, analyzing the surface behavior of such a simple system will illustrate how certain properties of the bulk liquid can affect surface properties. Moreover, most of the simulations of structurally asymmetric blends appearing in the literature have been athermal. Direct comparisons with the theory presented here will also help to clear up some discrepancies between the simulations and previous theoretical work.

For these purposes, we model the bulk response (as characterized by the functions $\hat{c}_{KK'}$) for an athermal blend of thread polymers using PRISM theory; this approach was pioneered by Curro and Schweizer.[22] PRISM theory is an extension of the RISM theory of Chandler and Andersen[19] to polymeric liquids. For effectively athermal homopolymer melts and blends, PRISM has been shown to be in quantitative agreement with simulations for the structure factor and radial distribution function;[18] hence, we expect to have reliable values for $\hat{c}_{KK'}(0)$ in the thread limit as well. As the site diameters are shrunk to zero, PRISM theory retains the finite-diameter hard-core exclusion effects of our original system in an approximate way by requiring that the chains not overlap:[17] that is, we require that $g_{KK'}(0) = 0$, where $g_{KK'}(r)$ is the radial distribution function between sites K and K' on different chains. The integrated strength of the effective interaction (i.e., including the effects of screening by other chains) between two such monomers is then set by $\hat{c}_{KK'}(0)$. (For purposes of comparison, it may be somewhat preferable to use the $\hat{c}_{KK'}(0)$ obtained directly from simulations of the true bulk athermal liquid; however, these quantities are generally not available.) Hence, the "packing" effects incorporated into the model account for only the coarse-grained effective interaction between monomers and will not capture the detailed oscillations in liquid structure on the monomer scale. Other local "packing" effects due to tacticity, chain shape, and anisotropic nematic-like interactions among chains with a finite bending rigidity (as may be present in simulations using such chain models) are also neglected in this approximation.

In the long chain ($N_K \gg 1$) limit, Curro and Schweizer find[22]

$$\hat{c}_{AA}(0) = \frac{1}{\gamma^2}\hat{c}_{AB}(0)$$

$$\hat{c}_{BB}(0) = \gamma^2\hat{c}_{AB}(0) \qquad (17)$$

where $\hat{c}_{AB}(0) < 0$ and $\gamma = b_B/b_A$. This says that the effective screened interaction is stronger with a monomer of the stiffer (higher b_K) component than with the more flexible (lower b_K).

The sign of the enrichment near a wall can be obtained by substituting eqs 17 into the general expression (16) given in the previous section. However, here we proceed alternatively by considering in more detail the effective fields $w_K(z)$ felt by each species. Using eqs 4, 10, and 17, we find that these effective fields have the form

$$w_A(z) = \frac{1}{\gamma}f(z)$$

$$w_B(z) = \gamma f(z) \qquad (18)$$

where

$$f(z) = \sqrt{\hat{c}_{AA}(0)\hat{c}_{AB}(0)}\,\Delta\rho_A(z) + \sqrt{\hat{c}_{BB}(0)\hat{c}_{AB}(0)}\,\Delta\rho_B(z) \qquad (19)$$

Substituting eq 18 into eq 9, we find that the functions $q_K(z,s)$ obey the equations

$$\gamma\frac{\partial q_A(z,s)}{\partial s} = \frac{b_A b_B}{6}\frac{\partial^2}{\partial z^2}q_A(z,s) - f(z)\, q_A(z,s)$$

$$\gamma^{-1}\frac{\partial q_B(z,s)}{\partial s} = \frac{b_A b_B}{6}\frac{\partial^2}{\partial z^2}q_B(z,s) - f(z)\, q_B(z,s) \qquad (20)$$

These equations become symmetric in A ↔ B once the monomer index s is rescaled by γ for A-chains and γ^{-1} for B-chains. As shown in section III, such a rescaling corresponds to a redefinition of a monomer. In the present case of athermal threads, however, this rescaling matches both the statistical segment lengths and effective interactions at the same time. At this level of description, the only remaining distinction between the two chains is in their radii of gyration, which give rise only to small surface segregation effects of order $O(N^{-1})$.[30] Otherwise, the (rescaled) equations for $q_A(z,s)$ and q_B-

(z,s) are identical, and there is no surface segregation due to conformational (structural) asymmetry for a strictly athermal blend.

In fact, this is a consequence of the form given for the species-dependent direct correlation functions in eqs 17: the strength of the effective interaction between two monomers is proportional to the square of their statistical segment lengths—the same scaling that controls the gradient term $(b_{\mathrm{K}}^2/6)\nabla^2 q_{\mathrm{K}}(\mathbf{r},s)$. It is, however, the balance between these same two terms that determines both the bulk total density healing length and the surface tensions of the pure components. Here, they are equal, and the conformational entropy (described by the gradient term) and packing forces (appearing in the effective, medium-moderated, interaction) precisely cancel. This result is identical to that found by Kumar *et al.* using the thread version of the wall-PRISM theory.[1]

This result is also consistent with what is observed in simulations: very little surface segregation is seen, and what little enrichment is observed favors the "stiffer" component.[1,10,11] The difference between what we predict here and what has been observed in simulation is probably due to differences in how the chain structure is modeled. As discussed above, the Gaussian nature of the model does not capture nematic-like interactions associated with finite bending rigidity. Including such effects would likely favor enrichment of the stiffer chain. At a free surface, local ordering is diminished; hence, our predictions should be more accurate for this case. Further, at a textured, rough, or otherwise nonflat surface, one might also imagine that such preferences may diminish or disappear. In fact such effects have been observed in mean-field calculations using lattice models of polymers near a surface with a soft potential.[1]

Table 1. Isothermal Compressibility and β Parameter of Typical Polyolefins ($N \gg 1$)[a]

polyolefin	κ_T ($\times 10^4$ MPa^{-1})	β^2 ($\times 10^2$ Å^{-1})
PE	10.9	12.1
PEP	11.5	8.1
hhPP	11.3	
i-PP		4.4*
a-PP	13.1	
PEB	11.7	
PEE		3.8

[a] Notation: hhPP, i-PP, and a-PP are atactic head-to-head, isotactic, and atactic polyproplylene, respectively; PEB is an alternating copolymer of ethylene and 1-butene. Compressibility values are for $T = 167$ °C and $P = 1$ atm. β parameter values are for $T = 25$ °C and $P = 1$ atm, except (*) which is at T=180 °C. We expect the β parameter value of i-PP at 25 °C to be slightly ($\sim$10 %) larger than its value at 180 °C. All compressibility data are from Krishnamoorti et al.,[29] and all β parameter data are from Sikka et al.,[6] except (*) which is from Weimann et al.[40]

V. Polyolefins: Attractive Interactions and Equal Compressibility

In the previous section we found that there is no or only weak surface segregation arising from structural asymmetry for an athermal polymer blend. Effects of conformational entropy, which favor the surface enrichment of the more flexible component, are canceled by packing forces that favor enrichment by the stiffer one. In this section we extend our analysis to include attractive forces between the polymer molecules, which must exist to provide cohesion for the polymer melt. We will focus here on polyolefins, as they have been well studied in recent experiments.[6,7]

The effect of attractive interactions enters our theory through the amplitudes $\hat{c}_{\mathrm{KK}'}(0)$ *via* the direct correlation functions $c_{\mathrm{KK}'}(\mathbf{r})$. Including attractive interactions within a liquid-state theory such as the one described here is nontrivial and has been the subject of much controversy in recent years.[23-27] Nevertheless, we can exploit a more direct path to determine the values of $\hat{c}_{\mathrm{KK}'}(0)$ from experimentally measured properties of polyolefins. The argument is as follows. First, it is known empirically that the volume change upon mixing for polyolefins is small.[29] That is, if we define equivalent pure-component site volumes for the two types of monomers, then the total site density $\bar{\rho}_0 \equiv \bar{\rho}_{\mathrm{A}} + \bar{\rho}_{\mathrm{B}}$ is approximately constant for any concentration $\bar{\rho}_{\mathrm{A}}$. Next, considering $c_{\mathrm{KK}'}(r)$ as a screened potential, one expects that the difference between $\hat{c}_{\mathrm{AA}}(0)$ and $\hat{c}_{\mathrm{BB}}(0)$ is smaller in the mixed state than in the pure state. In the pure state, the direct correlation amplitudes are related to the pure-component compressibilities $\kappa_{T\mathrm{A}}$ and $\kappa_{T\mathrm{B}}$ by[13]

$$\hat{c}_{\mathrm{AA}}(0)\Big|_{\bar{\rho}_{\mathrm{B}}\to 0} = -\frac{1}{\kappa_{T\mathrm{A}}(\bar{\rho}_{\mathrm{A}})^2}$$

$$\hat{c}_{\mathrm{BB}}(0)\Big|_{\bar{\rho}_{\mathrm{A}}\to 0} = -\frac{1}{\kappa_{T\mathrm{B}}(\bar{\rho}_{\mathrm{B}})^2} \qquad (21)$$

where we have taken the long chain limit, $N_{\mathrm{K}} \gg 1$. In Table 1, the pure melt compressibilities and β parameters of some of the more common polyolefins are listed.[6,28,29,40] One can see that the κ_T values for these polyolefins lie within 20% of each other. In comparison with the differences in the β parameters, this spread is small. With these considerations, we approximate the compressibilities as equal, and so

$$\hat{c}_{\mathrm{AA}}(0) \approx \hat{c}_{\mathrm{BB}}(0) \approx -\frac{1}{\kappa_T(\bar{\rho}_0)^2} \qquad (22)$$

at any concentration $\bar{\rho}_{\mathrm{A}}$. Here, κ_T is the compressibility of a pure type-A or -B melt. The number of independent $\hat{c}_{\mathrm{KK}'}(0)$'s is thus reduced from 3 to 2.

With these expressions for the amplitudes, our effective fields $w_{\mathrm{K}}(z)$ become

$$w_{\mathrm{K}}(z) = \sum_{\mathrm{K}'}\left[\chi(1-\delta_{\mathrm{KK}'}) + \frac{1}{\kappa_T\bar{\rho}_0}\right]\frac{\Delta\rho_{\mathrm{K}'}(z)}{\bar{\rho}_0} \qquad (23)$$

where we have used the following definition of the Flory χ parameter:

$$\chi = \frac{\bar{\rho}_0}{2}(\hat{c}_{\mathrm{AA}}(0) + \hat{c}_{\mathrm{BB}}(0) - 2\hat{c}_{\mathrm{AB}}(0)) \qquad (24)$$

This is the Helfand–Tagami[5] expression for the effective field. In other words, the approximation of equal compressibility reduces our theory to the Helfand and Tagami "self-consistent field" theory.[5] In previous works, we have shown numerically[8] and analytically[4,30] that the form (23) for $w_{\mathrm{K}}(z)$ when $\chi = 0$ leads to the surface enrichment of the component having the smaller "beta" parameter $\beta_{\mathrm{K}}^2 = b_{\mathrm{K}}^2\bar{\rho}_0/6$. In other words, in the absence of a Flory χ interaction, the more "flexible" component is enriched at a neutral surface. This result can also be found directly by the use of eq 16.

It is clear from eq 16 that a nonzero χ value affects segregation also. However, using equilibrium data for the polyolefins, one finds that, while the first term is of order unity, the second term in eq 16 is of order 10^{-3} and can effectively be neglected.[31] Since data from

Table 1 justify furthermore the approximation of equal compressibility for these polyolefins, the asymmetry in the first term in (16), and hence the surface segregation behavior, is therefore controlled by the differences in the β parameters.

VI. Pure Component Theory

It is a common hope in material science to be able to predict the properties of a multicomponent system using just information about the properties of the pure components. An example in the polymer field is the frequent use of regular solution (Hildebrand) theory to assess the miscibility of a large number of polymer blends.[32,33]

A corresponding question for polymers near surfaces is how well can knowledge of the pure component surface tensions yield information on the surface segregation behavior of a blend? This question was addressed by Poser and Sanchez,[34] Dee and Sauer,[35] and more recently by Wu and Fredrickson[4] who presented a scaling argument based on the ansatz that the amplitude of the effective surface segregation field, at least for weak segregation, is directly proportional to the difference in pure-component surface tensions. Moreover, the surface tension is taken to be proportional to the product of an interfacial width $\xi_h \sim \beta(\kappa_T)^{1/2}$ (the healing length of the melt) and an interaction/cohesive free energy density, α. The trends given by this pure-component scaling theory were consistent with a perturbative analysis of the SCF equations as well as with recent experiments on polyolefins by Bates' group.[6] It was shown furthermore that for conformationally symmetric blends with differing interaction densities, the scaling theory reduces to the Hildebrand theory; i.e., it predicts that the lowest cohesive energy density component is preferred at the surface.

Here, we review the scaling argument for polyolefins, demonstrate how this analysis can be equally applied to the athermal blend, and then briefly discuss its applicability to other cases. In our present notation, the surface tension of a homopolymer melt at an air or vacuum interface can be calculated within SCF theory to be[4]

$$\gamma \sim -\xi_h \hat{c}(0)\bar{\rho}^2 \qquad (25)$$

where the subdominant ideal gas term has been dropped. (This expression can also be derived from CMS density functional theory.[36]) Making use of eq 21 we have $\gamma \sim \beta/(\kappa_T)^{1/2}$. Hence, the difference $\Delta\gamma$ in surface tension between pure melts of type A and type B is

$$\Delta\gamma \equiv \gamma_A - \gamma_B \sim \alpha_A \xi_{hA} - \alpha_B \xi_{hB} \sim \beta_A/\sqrt{\kappa_{TA}} - \beta_B/\sqrt{\kappa_{TB}} \qquad (26)$$

which is eq 1.1 of Wu et al.[4] Here, the parameters β_K and κ_{TK} must be evaluated at the same temperature and pressure. Now, if $\Delta\gamma < 0$ then the type-A component will be enriched at the surface; if $\Delta\gamma > 0$, then the type-B component will be enriched. One sees immediately for the case of nearly equal pure component compressibilities that this equation predicts surface segregation to be determined by the difference in the β parameters. This result is consistent with those of section V, the experiments on the polyolefin diblocks, and the air−surface observations in the copolymer blends.

We now turn to the athermal blend. In order to compare the free energies of the pure-component melts, we need to examine the two at equal pressures. The pressure within SCF theory is given (again for $N \gg 1$) by[4]

$$P \sim -\hat{c}(0)\bar{\rho}^2 \qquad (27)$$

With eq 21, this implies that the compressibilities are equal, $\kappa_{TA} = \kappa_{TB}$, and also the interaction densities, $\alpha_A = \alpha_B$. (We note that for general polymer blends with attractions, the pressure, a differential quantity, will not simply be equal to the interaction density, an integrated quantity.) Using thread-PRISM, Schweizer and Curro find (for long chains, $N \gg 1$)[17]

$$\hat{c}(0) \sim \bar{\rho} b^6 \qquad (28)$$

From this, the pressure

$$P \sim {\rho_b}^3 b^6 \sim \beta^6 \qquad (29)$$

is seen to depend only upon β. Therefore, from (26), we find that $\Delta\gamma = 0$, predicting no surface enrichment for a structurally asymmetric athermal blend of thread polymers, in agreement with our predictions of section IV. We comment that while β usually can be thought of as a local monomer aspect ratio, as threads, β will depend only upon R_g and ρ_{mol}. That is, by lowering the melt density, β is effectively reduced. Thus two conformationally asymmetric polymers of equal R_g have identical coarse-grained descriptions when compared at the same molecular density (i.e., same β). The condition of equal pressures thus effectively renders the two components indistinguishable. However, for blends of pure-component melts of comparable cohesive energies, such as the polyolefins and the case examined by Wu and Fredrickson, the interaction densities are indeed comparable or equal at equal pressures, and so the surface segregation is controlled by the healing length or, equivalently in this case, by the β parameters.[30]

It is interesting to see what the pure component theory predicts for a blend of long and short polymers of the same type. Dee, Ougizawa, and Walsh[28] have made a number of measurements of the compressibility of various linear hydrocarbons. We compare the properties of two: $C_{44}H_{90}$ and HDPE with molecular weights of 619 and 28000, respectively. From their Figure 2, the densities of C_{44} and HDPE at 167 °C and 0.1 MPa are 0.741 and 0.775 g/cm^3, respectively. From their Figure 4, the compressibilities at the same temperature and pressure are 1.425×10^{-3} MPa^{-1} and 1.18×10^{-3} MPa^{-1}, for C_{44} and HDPE, respectively. The statistical segment lengths are about the same. With these values we predict from eq 26 that C_{44}, the shorter polymer, will have the smaller surface tension. This result is consistent with many experiments[37] that show that the surface tension of polymers increases with molecular weight. Hence, the pure-component theory predicts that the shorter polymer will be enriched, as is consistent with recent experiments[35] and theory.[30,35]

The pure-component theory is therefore in agreement with the results above for athermal blends and polyolefin systems. However, as stated above, the theory in this paper uses as input the mixed-state interactions, and so a full test or comparison of the pure-component ansatz (of a surface field proportional to differences in surface tension) would require a prescription for determining the relation between mixed-state interactions and those in the pure states.

VII. Discussion and Conclusions

We have presented a coarse-grained model for describing polymer blends with the purpose of examining the effect of the bulk properties of conformational asymmetry and compressibility on surface segregation. Effects of packing and cohesive energy are captured by a few parameters—the integrated strength of the direct correlation function—which can be related to osmotic compressibilities. This model, which can be derived from density functional theory, reduces to the Helfand–Tagami theory with a suitable rescaling of the definition of a monomer. By generalizing the perturbative analysis used in ref 4 to the case of a nonzero Flory χ parameter, we have derived a general expression that determines the sign of surface segregation for arbitrary asymmetry in conformational properties and interaction potentials between short-branched blend components. This analysis can be extended to long-branched chains following the methods of Wu and Fredrickson.[38]

The predictions of this generalized theory are consistent with our previous theoretical work,[2,4,8] as well as experiments on polyolefin diblock copolymers,[6] and, apparently, polyolefin random copolymer blends at air surfaces.[7] In particular, we show that the assumption of equal compressibility used in these theories was appropriate for the polyolefin systems considered. Moreover, the present theory also gives predictions in accord with the simulations and PRISM theory showing little or no surface segregation for athermal blends,[1,10,11] when the effect of compressibility (reflecting packing considerations) is taken into account. In particular, the prediction of a thread analysis of wall-PRISM by Kumar *et al.* is identical to ours. Their explanation is also that the absence of segregation follows from invariances in the thread theory. The slight preference for "stiff" (in the sense of bending rigidity) polymers seen in the simulations might be accounted for by modeling the chains as semiflexible instead of Gaussian, thereby incorporating nematic-like interactions with the wall, along with retaining the finite hard-core and discrete nature of the monomers.

Surface segregation arises from a competition between conformational entropy, packing forces, and bulk cohesive energy (as well as other surface-specific effects). Differences in the conformational entropy of the two chains favors the enrichment of the more flexible component, while differences in packing arising from differences in chain structure favor the enrichment of the stiffer component. Effects of packing and cohesive energy enter through the amplitudes $\hat{c}_{KK'}(0)$. Equal compressibility, κ_T, of the pure polyolefin melts implies that differences in packing are canceled out by differences in cohesive energy. This cancelation leaves surface segregation to be determined primarily by conformational entropy. On the other hand, one could interpret the cancelation of the entropic effects of chain conformations and packing for the athermal blend to mean that effects of bulk cohesive energy, i.e. enthalpy, determine the surface segregation for the real polyolefin blend, a view expressed by refs 1, 10, and 11. In some sense, it is perhaps a question of how one views the combination of these three effects. A test of this explanation would be to check if the introduction of monomer–monomer attractions to the athermal blend in simulations[1,10,11] causes the measured amplitudes $\hat{c}_{KK}(0)$ to be nearly equal. In any case, it is instructive that the competing influences can be effectively incorporated into a coarse-grained model with a few simple parameters, which in some cases can be determined empirically through the use of experimental or simulation data.

An interesting example of the possible effect that differences in molecular architecture can have on surface segregation is given by a comparison of the experiments of the Bates group on diblock copolymers[6] with those of the Klein group on random copolymer blends.[7] Both systems are polyolefins, and both groups find that the more "flexible" component is preferred at the air–polymer surface. However, while the Bates group finds the same behavior at a solid substrate (silicon, silver, and quartz being those used), the Klein group finds no apparent segregation there (silicon and gold being those used.) The difference in segregation for the copolymer blend can be attributed to the increase in packing near a solid substrate effectively eliminating any depletion region near the surface (upon which the coarse-grained mechanism discussed herein for favoring the lower β component depends). If this is true, it remains, then, to understand why the diblock copolymers *are* found to segregate at solid substrates. A possible explanation is given by recent work of Carignano and Szleifer[39] in which a type of self-consistent field theory is used to examine segregation of a thin film of strongly stretched lamellar diblock copolymers. They find that the lamellar ordering tends to frustrate packing at the surface and that the more "flexible" block is preferred at the surface even though their system might be considered athermal. This explanation, however, is possibly incomplete, since the diblock experiments showed the "flexible" polymer enriched at the surface even for samples in the *disordered* (weak-stretching) phase, where one might expect the above mechanism to be weak or inoperative. In any case, both experiments and theory do indicate that molecular architecture can play an important role in surface segregation.

Finally, we note that the results of the SCF theory presented herein are predicted—with one exception—by a simple pure component scaling argument presented by Wu et al.[4] postulating that the effective surface composition field is proportional to the difference in pure-component surface tensions. The sole exception, that the minority phase is enriched at the surface when $\chi \neq 0$ for two otherwise identical polymers, is outside the scope of the simple scaling theory. While this effect is predicted to be negligible for polyolefins, it may play a larger role in other polymeric systems.

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Appendix: Perturbative Analysis of Surface Segregation for Nonzero χ

We consider here perturbative solutions in the small parameters $(\epsilon - 1)$ and χ of the differential equation (9) for $q_K(z,s)$ with the effective field given by (23). Our approach is a straightforward extension of that in ref 4 to which the reader is directed for further details. In particular, we consider perturbations about the symmetric reference (denoted by a subscripted 0) with $b_A = b_B = b$ such that

$$q_K(z) = q_0(z) + (\epsilon - 1)\bar{q}_K^{\epsilon}(z) + \chi\bar{q}_K^{\chi}(z) \qquad \text{(A1)}$$

where the terms involving the first-order corrections in ϵ (or χ) have an overbar and carry a superscripted ϵ (or χ). Here, we are considering only the large N_K limit, so the "q" functions are independent of the contour variable s (ground-state limit). From (8), we also have

$$\rho_K(z) = f_K\rho_0(z) + (\epsilon - 1)\bar{\rho}_K^{\epsilon}(z) + \chi\bar{\rho}_K^{\chi}(z) \qquad \text{(A2)}$$

with

$$\bar{\rho}_{\mathrm{K}}^{\epsilon}(z) = 2\bar{\rho}_0 q_0(z)[\bar{q}_{\mathrm{A}}^{\epsilon}(z) + \bar{q}_{\mathrm{B}}^{\epsilon}(z)]$$

$$\bar{\rho}_{\mathrm{K}}^{\chi}(z) = 2\bar{\rho}_0 q_0(z)[\bar{q}_{\mathrm{A}}^{\chi}(z) + \bar{q}_{\mathrm{B}}^{\chi}(z)] \qquad \text{(A3)}$$

and $f_{\mathrm{K}} = \bar{\rho}_{\mathrm{K}}/\bar{\rho}_0$. In the latter pair of equations, we have invoked a ground-state approximation, implying a choice of $w_{0\mathrm{K}}$ that sets the zero of potential (in the bulk) to zero for each component. Moreover, in the ground state, we have the well-known profiles

$$q_0(z) = \tanh(z/\xi)$$

$$\rho_0(z) = \bar{\rho}_0 \tanh^2(z/\xi) \qquad \text{(A4)}$$

where

$$\xi = \frac{b}{\sqrt{3\hat{c}(0)\bar{\rho}_0}} \qquad \text{(A5)}$$

is the bulk correlation length.[4,30]

To first order in $(\epsilon - 1)$ and χ, we find

$$\left\{\frac{\partial}{\partial s} - \frac{b^2}{6}\frac{\partial^2}{\partial z^2} + \hat{c}(0)[\rho_0(z) - \bar{\rho}_0] + \frac{\chi}{\rho_0}[\rho_{K'}(z) - f_{K'}\bar{\rho}_0]\right\} \times [(\epsilon - 1)\bar{q}_K^{\epsilon}(z) + \chi\bar{q}_K^{\chi}(z)] = (\epsilon - 1)\left[\theta_K\frac{b^2}{12}\frac{\partial^2}{\partial z^2}q_0(z) - \hat{c}(0)\bar{\rho}_K^{\epsilon}(z)q_0(z)\right] - \frac{\chi}{\bar{\rho}_0}f_{K'}[\rho_0(z) - \bar{\rho}_0]q_0(z) \qquad \text{(A6)}$$

where θ_{K} is an Ising-like variable with values $\theta_{\mathrm{A}} = 1$ and $\theta_{\mathrm{B}} = -1$ and $\mathrm{K}' = \mathrm{B}$ if $\mathrm{K} = \mathrm{A}$ and vice-versa. The surface segregation was shown previously[4] to be determined by the difference $\bar{q}_{\mathrm{A}}^{\epsilon}(z) - \bar{q}_{\mathrm{B}}^{\epsilon}(z)$, with the strength of the effective surface field being given by the coefficient $(\epsilon - 1)$ of the first inhomogeneous source term $(\epsilon - 1)\theta_{\mathrm{K}}$-$(b^2/12)(\partial^2 q_0(z)/\partial z^2)$ on the right hand side of (A6). (The adjacent term involving $\hat{c}(0)$ turns out to be irrelevant for the sign of the segregation.) The question now is to find the same term for the first-order contribution due to χ. However, we see from the above that the source term involving χ is conveniently of the same form, since

$$\frac{\partial^2}{\partial z^2}q_0(z) = \frac{2}{\bar{\rho}_0\xi^2}[\rho_0(z) - \bar{\rho}_0]q_0(z) \qquad \text{(A7)}$$

for the reference ground-state functions given in (A4). By comparing the coefficients of the source terms and using (A5), one arrives at (15) for the expression controlling the strength of the surface field and hence the sign of surface segregation for weak enrichment. For stronger segregation, i.e., large values of expression 15, we expect to find saturation of the preferred component at the surface.

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