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Properties of Random Multiblock Copolymer Melts near Surfaces

James P. Donley[†] and Glenn H. Fredrickson*

*Department of Chemical and Nuclear Engineering and Materials Department,
University of California, Santa Barbara, California 93106*

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ABSTRACT: A mean-field theory is presented to describe the surface tension and interfacial profile of compositionally homogeneous, random A–B multiblock copolymer melts in contact with air or a solid substrate. The copolymer model accounts for variations in average composition and block sequence distribution and reduces to a model for a statistical copolymers as the block size approaches that of a monomer. It is found that, to prevent unphysical behavior of the surface tension and profile, one must explicitly incorporate into the theory the effect of the surface on the chain conformations. This is done by deriving an expression for the free energy of a random copolymer melt in contact with a neutral impenetrable surface. With this free energy we find that, depending upon the type of chemical correlations between successive segments and the temperature, the composition profile can either be oscillatory or monotonic. Further, “blocky” copolymers with a tendency for repeated segments of A or B are predicted to have a lower surface tension than copolymers with a tendency for alternation of A and B segments.

I. Introduction

The interfacial properties of polymer melts and solutions are important in many industrial processes, such as those involving coating, film blowing, or mixing steps. Interfacial tension also plays a key role in microstructural evolution during the processing of polymer blends. Consequently, a great deal of effort has been focused on developing a fundamental understanding of the factors that control interfacial tension in polymeric systems. Modification of interfacial properties, e.g., by the addition of copolymers, has proven to be a powerful method for manufacturing materials with a broad range of controlled morphologies.

For the above reasons, there has been much scientific interest in recent years in the interfacial properties of polymeric systems.¹ While a large number of experimental and theoretical studies have appeared that address the thermodynamic properties of internal and external (surfaces) interfaces in homopolymer melts and solutions,^{1–8} much less attention has been paid to the interfacial properties of copolymers. A notable exception is recent work on the compositional ordering of diblock copolymer melts near a free (e.g., air) surface or solid substrate.^{9–14} In spite of the commercial significance of statistical copolymers (e.g., SBR) and ill-characterized block copolymers (e.g., polyurethanes), few systematic investigations of their interfacial properties have been reported.^{15–19}

Recently, Fredrickson, Milner, and Leibler (FML) have presented a theory that describes the bulk thermodynamic properties of statistical copolymers and random block copolymer melts in a mean-field approximation.²⁰ A similar analysis for the special case of ideal random copolymers has been done by Shakhnovich and Gutin²¹ and Dobrynin and Erkumovich.²² In a previous paper,²³ we generalized the FML theory to investigate the interfacial tension and composition profile of such materials at an air interface or in the vicinity of a solid substrate. This analysis was restricted to blocky copolymer melts, i.e., copolymers with a tendency for repeated segments of A or B along the chain backbones. Here, we extend this analysis to describe the almost complete spectrum of possible chemical correlations from alternating copolymers

to very blocky copolymers. In order to simplify the analysis, we restrict consideration to conditions for which the bulk melt is compositionally homogeneous. Particularly for the case of statistical copolymers, this regime encompasses much of the experimentally accessible phase diagram.

The simplest theoretical description of an A–B copolymer melt at a surface¹⁵ ignores any difference between the bulk and surface compositions of the melt. The interfacial composition profile is thus assumed to be flat and (neglecting nonideal mixing effects) the interfacial tension is given by the linearly additive expression

$$\gamma = f\gamma_A + (1-f)\gamma_B \quad (1)$$

where γ_A and γ_B are the pure component surface tensions and f is the copolymer composition (i.e., volume fraction of A). We assume equal monomer volumes for A and B. This expression is appealing because it only involves the pure component surface tensions and the bulk composition and is independent of the arrangement of the A and B monomers along the chains. However, eq 1 is rarely found to be obeyed in practice.¹⁶ Because one of the two components normally has a lower surface tension, e.g., species A, there are enthalpic and (possibly) entropic benefits to be gained locally by placing an excess of A monomers in the surface layer. Since these monomers are embedded in the polymer chains in more or less random sequences, there is a configurational entropy penalty to be paid for such nonuniform placement of species A. Nevertheless, as we shall demonstrate below and has been seen in previous calculations for diblock copolymers,¹⁰ the enthalpy benefit outweighs the entropy penalty so that nonuniform surface composition profiles are generally to be expected. It is important to point out that because the configurational entropy penalty at the surface depends on the statistical arrangement of A and B monomers along the chains, the composition profile and interfacial tension are sensitive functions of the comonomer sequence distribution. Thus, we find different expressions for the interfacial tensions of alternating copolymers, ideal statistical copolymers, and “blocky” random copolymers.

This work is organized as follows. In section II, we briefly review the FML model of random multiblock copolymer (RBCP) melts and the melt phase behavior in the bulk. Then, we introduce the usual¹⁶ mean-field description of the surface tension of polymer melts. We then argue that,

* Present address: Advanced Materials Laboratory, University of New Mexico, 1001 University Blvd. SE, Albuquerque, NM 87106.

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for RBCP's, this description is incomplete. More precisely, we argue that, for a physically correct theory, the form of the melt free energy per area of surface must include effects due to restrictions on chain conformations near the surface. This free energy is derived in Appendix B. With this free energy in hand, we then derive expressions for the surface composition profile and the surface tension. We find that, depending upon the type of chemical correlations on the chains and the temperature, the profile can be either monotonic or oscillatory. Furthermore the surface tension is found to be greatest for alternating copolymers and smallest for blocky random copolymers. Finally, in section III, we adapt our RBCP theory to describe the surface behavior of homopolymer blends and diblock copolymers and compare our results with those of previous investigations.

II. Model and Analysis

Our model random multiblock copolymer melt is defined as follows. We consider an incompressible assembly of A-B copolymers in contact with a planar surface. Each chain consists of a stochastic sequence of Q flexible segments; a segment is either a polymerized sequence of M monomers of type A or M monomers of type B. We ignore effects associated with overall chain-length polydispersity; hence, every chain has exactly $N = QM$ monomers. The radius of gyration R_M of a segment is assumed to obey Gaussian statistics in the bulk and to be the same for both types of segments. Thus, $R_M = \bar{a}_{AB}(M/6)^{1/2}$, where \bar{a}_{AB} is the statistical segment length of an A or B segment (assumed equal). Likewise, each chain has a radius of gyration $R_N = \bar{a}_{AB}(N/6)^{1/2}$. Besides the constraint of incompressibility, which crudely accounts for the repulsive part of the intermonomer potential, differences in the attractive parts of the A-A, A-B, and B-B potentials are described by the conventional Flory χ parameter. In practice, the Flory parameter will also have an entropic component that derives from the detailed liquid structure on the monomer scale.

The stochastic distribution of A and B segments along each chain is described by a first-order Markov model of random copolymerization²⁴ as in FML.²⁰ In this model the distribution of copolymeric species is described by two parameters: f , the average volume (or mole) fraction of type A segments incorporated into the chains, and $\lambda = p_{AA} + p_{BB} - 1$, where p_{ij} is the conditional probability that a type j segment on a chain is immediately followed by a type i segment. The copolymerization is assumed to be carried out under continuous, steady-state conditions, so that f and λ do not vary with contour position on the chains. The minimum value of λ , -1, corresponds to a melt of perfectly alternating A-B multiblock copolymers. In contrast, the maximum value of λ , +1, corresponds to a mixture of A and B homopolymers, each of degree of polymerization N and a fraction f of the chains being of type A. The intermediate case of $\lambda = 0$ describes an "ideal" random multiblock melt, in which there are no correlations between the chemical identities of successive segments along the chains. Cases of $\lambda > 0$ thus correspond to blocky copolymers, while cases of $\lambda < 0$ correspond to melts with a tendency for alternation of A and B segments. Expressions for copolymerizations carried out under steady-state conditions that explicitly relate f and λ to the feed composition, f_0 , and the two monomer reactivity ratios, r_A and r_B , are given in FML. Finally, we note that a statistical (or random) copolymer model is obtained as a special case of the above random multiblock model by setting $M = 1$.

In the following analysis we restrict consideration to situations in which the bulk copolymer melt is composi-

tionally homogeneous. For the present purpose, this requires that χ be restricted to values that do not exceed the stability limit of the homogeneous phase, $\chi = \chi_s(f, M, Q, \lambda)$. For $\lambda > -0.268$ this threshold was shown by FML to describe the onset of liquid-liquid phase separation and is given to leading order in Q^{-1} by

$$\chi_s = \frac{1 - \lambda}{2f(1 - f)(1 + \lambda)M} \quad (2)$$

For $\lambda < -0.268$ the homogeneous phase loses stability to a microphase (without long-range order) at $\chi = \chi_s$. As the expression for this threshold is more complicated, we refer the reader to FML. The special case of $\lambda = \lambda_L = -0.268$ corresponds to a Lifshitz point at which the tendencies for liquid-liquid separation and microphase separation are precisely balanced. As will become apparent below, the qualitative features of the surface composition profile depend strongly upon λ .

The above idealized copolymer melt is placed in contact with a flat, impenetrable surface of macroscopic area S . The coordinate perpendicular to the surface is denoted z , with the surface located at $z = 0$. The thickness of the melt perpendicular to the surface is denoted L , so the melt volume is given by $V = SL$. (L will be taken to infinity at the end of the calculation in order to describe a semiinfinite slab of melt.) Once in contact with the surface, the melt adjusts its spatial composition such that its free energy is minimized. Following FML, we describe the copolymer concentration field by $m(\mathbf{x}) = \phi_A(\mathbf{x}) - f$, where ϕ_A is the local volume fraction of type A monomers. In the bulk homogeneous phase of a copolymer melt, $m(\mathbf{x})$ vanishes identically. The reequilibration of the melt after being brought in contact with the surface produces a nonvanishing interface profile $m(z)$, which decays to zero far from the surface. Since the bulk melt is assumed to be homogeneous, we expect, from translational invariance in the surface plane, that the composition profile is a function only of the distance z from the surface; thus $m(\mathbf{x}) = m(z)$.

The surface tension, or excess free energy per unit surface area, of the melt is assumed to be given by the expression

$$\gamma[m] = \gamma_0(f) + F_s[m]/S + F_b[m]/S \quad (3)$$

where γ_0 and F_s are the changes in the free energy due to surface fields acting on the melt. These will be discussed in more detail below. $F_b[m]$ is the bulk free energy of the melt in excess of the free energy of a bulk homogeneous phase. An explicit expression for F_b , developed as an expansion in $m(z)$ to fourth order, was given by FML. If the profile $m(z)$ decays over a length scale $\xi \ll R_N$, then one can show that the quadratic term in F_b gives the dominant contribution to the free energy for surface excesses $m_1 = m(0) < 1$. As we shall demonstrate below, this condition on the decay of $m(z)$ is met for high molecular weight polymers, $Q \gg 1$, except in the extreme vicinity of the stability limit. We will restrict ourselves here to weak surface fields (a restriction on F_s) so that $m_1 \ll 1$, and, subsequently, we will approximate F_b by retaining only its quadratic term.

In what follows, we will scale all lengths in terms of the segment radius of gyration R_M and all energies in terms of $k_B T$, where k_B is Boltzmann's constant and T is the absolute temperature.

For the slab geometry above, the representation of F_b in real space is

$$F_b[m] = \frac{SR_M}{2v} \int_0^L dz_1 \int_0^L dz_2 \Gamma_2(z_1, z_2) m(z_1) m(z_2) \quad (4)$$

with

$$\begin{aligned}\Gamma_2(z_1, z_2) &= \int_k \int_q e^{ikz_1} e^{iqz_2} \frac{1}{Mf(1-f)} \Gamma(q) \delta(k+q) \\ \Gamma(q) &= Mf(1-f) \left[\frac{1}{G_2(q)} - 2\chi \right] \quad (5)\end{aligned}$$

Here, $\Gamma_2(z_1, z_2)$ is the two-point vertex function, and $G_2(q)$ is the noninteracting two-point correlation function, which has a form given in Appendix A. v is the effective monomer volume, and $\tilde{L} = L/R_M$ is the slab thickness in dimensionless units. Also, $\int_k = (1/2\tilde{L}) \sum_k \simeq \int_{-\infty}^{+\infty} dk / 2\pi$, where \sum_k denotes a sum over all reciprocal lattice vectors k for the interval $-\tilde{L} < z < \tilde{L}$. We note that FML is a "weak segregation theory". That is, in their theory $m(\mathbf{x})$ is assumed not to depart very much from zero, and consequently any chain stretching caused by large gradients in $m(\mathbf{x})$ is negligible. Thus, this vertex function Γ_2 is computed in an RPA²⁵ approximation.

To simplify the calculations, we have found it useful to approximate $\Gamma(q)$ by

$$\Gamma(q) \simeq \Gamma_A(q) = \frac{a}{q^2 + b^2} + cq^2 + d \quad (6)$$

A scheme for determining the coefficients in Γ_A is given in Appendix A, along with a discussion of the accuracy of the method. Within this scheme, c is a constant, a and b are functions only of λ , and d is a function of λ and the reduced temperature $\tau = 1 - \chi/\chi_s$, where $\chi_s = \chi_s(M, f, \lambda)$ is the value of χ at the spinodal. In $\Gamma_A(q)$ there are two length scales, \sqrt{c} and $l = 1/b$. l is strongly λ dependent with $l \rightarrow \infty$ as $\lambda \rightarrow -1$ and $l \rightarrow 1/4$ as $\lambda \rightarrow 0$. For $\lambda < 0$, l can be thought of as an "antiferromagnetic" correlation length that is a measure of the characteristic size of alternating A-B-A-B regions on the chains. For $\lambda \geq 0$, the Lorentzian term in $\Gamma_A(q)$ gives a small correction to F_b , and so we do not attach any physical significance to $l = 1/b$ for these values of λ .

In real space, this approximation gives F_b the form

$$F_b[m] = \frac{SR_M}{2vMf(1-f)} \left\{ \int_0^L dz \left[m^2(z) d + \left(\frac{dm}{dz} \right)^2 c \right] + \int_0^L dz_1 \int_0^L dz_2 \frac{a}{2b} e^{-b|z_1-z_2|} m(z_1) m(z_2) \right\} \quad (7)$$

The second term in eq 3, F_s , is due to energetic and entropic effects at the surface of the melt. We express this as $F_s = F_s^E + F_s^S$, where F_s^E and F_s^S correspond to the contribution to F_s from the energetic and entropic effects, respectively. The energetic contributions could, for example, be due to exchange or van der Waals interactions. We assume that these interactions are of a range which is smaller than the characteristic decay length of the profile $m(z)$. In such cases, we can approximate F_s^E as having the form

$$F_s^E[m] = \frac{S}{v} \int_0^L dz f_s(m) \delta(z) \quad (8)$$

Following previous work,^{6,26} f_s is assumed to have the form

$$f_s(m) = -\bar{\mu}m - \frac{1}{2}gm^2 \quad (9)$$

where $\bar{\mu} = \mu_1 + gf$. In this expression, μ_1 is a surface potential field that is expected to scale in proportion with the difference in pure component surface tensions, $\gamma_B - \gamma_A$, and g parametrizes the change in the interaction energies of the monomers at the surface. μ_1 and g are phenomenological parameters but can be obtained from experiment by using a method outlined by Jones et al.²⁶

It is important to note that μ_1 and g , like the bulk Flory parameter, χ , are supposedly properties of the monomers and not of the polymeric or copolymeric nature of the system; hence, determining these parameters for one type of A-B melt, in principle, determines them for all copolymer and homopolymer melts that contain the same two monomers. Finally, we note that $\gamma_0(f)$ appearing in eq 3 is the surface tension of a fictitious melt with $m(z) = 0$ (no surface excess or depletion of A monomers). For the special case of $g = 0$, γ_0 is given by eq 1, i.e., $f\gamma_A + (1-f)\gamma_B$. In general, however, the nonideal thermodynamics of the mixture, as crudely parameterized by g and χ , will render γ_0 a nonlinear function of f .

In a previous report on polymer blends, we have shown that a difference in statistical segment lengths, \bar{a}_A and \bar{a}_B , of the two species gives rise to an entropic interaction of the surface with the melt.²⁷ The cause of this interaction is that, near the surface, the chains have restricted conformations. This reduction in conformational entropy near the surface is greater, the larger the segment length is, and hence the chains with the smaller statistical segment length are entropically favored to be near the surface. In the present work, the statistical lengths of the two subblocks A_M and B_M are the same, and so this term will not be present in $F_s^S[m]$. However, the long-range nature of polymer backbone correlations gives rise to an additional entropic interaction of the surface with the melt. In Appendix B, we derive an expression for the free energy of a RBCP melt in contact with a neutral impenetrable surface. With the approximate form for $\Gamma_2(q, k)$ given by eq 6, we find that

$$F_s^S[m] = \frac{SR_M}{2vMf(1-f)} \int_0^L dz_1 \int_0^L dz_2 \frac{a}{2b} e^{-b(z_1+z_2)} m(z_1) m(z_2) \quad (10)$$

It is easy to show that such a term is necessary because, without it, we find that the bulk contribution to the surface tension is negative. This result implies that any nonzero surface field $\bar{\mu}$ will cause complete saturation of the surface with A or B monomers, which is clearly unphysical behavior. The problem arises because the third term in F_b is strongly nonlocal. Indeed, the nonlocal function $\exp(-b(z_1 + z_2))$ in F_s^S acts as an "image" potential of the function $\exp(-b|z_1 - z_2|)$ in F_b . That is, the free energy for a half-infinite slab in contact with an impenetrable neutral surface is equivalent (to within a factor of 2) to the free energy of a bulk melt with the order parameter $m(z)$ symmetric about $z = 0$.

With the above ingredients in our theory, we are now ready to determine the surface tension. We first need to obtain the equilibrium composition profile $m(z)$. In equilibrium, we require that

$$\frac{1}{R_M} \frac{\delta \gamma[m]}{\delta m(z)} = \text{constant} \equiv \mu \quad (11)$$

in the bulk. Here, $\delta/\delta m(z)$ is a functional derivative with respect to the concentration at position z . With eqs 6, 8, and 10, this relation leads to the following integrodifferential equation for $m(z)$:

$$\frac{1}{vMf(1-f)} \{ m(z) d - m''(z) c + \int_0^L dz_1 H(z, z_1) m(z_1) \} = \mu \quad (12)$$

where

$$H(z_1, z_2) = \frac{a}{2b} [e^{-b|z_1-z_2|} + e^{-b(z_1+z_2)}]$$

Next, we assume that $L \gg \xi$ and $|\lambda| < 1$, so that a large

reservoir of copolymers of many sequences exists in the slab. As a result, we can impose the boundary condition $m(z) \rightarrow 0$ as $z \rightarrow \bar{L} \rightarrow \infty$, which is consistent only with $\mu = 0$.

The solution to eq 12, with the above boundary condition at $z = \bar{L} \rightarrow \infty$, is

$$m(z) = \frac{m_1}{\zeta} [\sigma_2(b^2 - \sigma_1^2) \exp(-\sigma_1 z) - \sigma_1(b^2 - \sigma_2^2) \exp(-\sigma_2 z)] \quad (13)$$

with

$$\zeta = (\sigma_2 - \sigma_1)(b^2 + \sigma_2 \sigma_1) \quad (14)$$

and $m_1 = m(0)$. Here, σ_1 and σ_2 are complex with $\text{Re}(\sigma_1)$ and $\text{Re}(\sigma_2) > 0$ and are independent roots of the equation

$$d - c\sigma^2 - \frac{a}{\sigma^2 - b^2} = 0 \quad (15)$$

The solution for σ has four roots and four forms depending upon the value of λ :

$$\sigma = \begin{cases} \pm\tilde{\sigma}[1 \pm (1 - \omega)^{1/2}]^{1/2}, & \lambda > \lambda_L, \omega < 1 \\ \frac{\pm\tilde{\sigma}}{\sqrt{2}}[(\sqrt{\omega} + 1)^{1/2} \pm i(\sqrt{\omega} - 1)^{1/2}], & \lambda > \lambda_L, \omega > 1 \\ \pm\psi[(\varphi + 1)^{1/2} \pm i(\varphi - 1)^{1/2}], & \lambda < \lambda_L, \Gamma(q^*) > (q^*)^2 \\ \pm\psi[(\varphi - 1)^{1/2} \pm i(\varphi + 1)^{1/2}], & \lambda < \lambda_L, \Gamma(q^*) < (q^*)^2 \end{cases} \quad (16)$$

where

$$\begin{aligned} \omega &= \frac{2\Gamma(1 - 2\Gamma')}{\Gamma''\tilde{\sigma}^4} \\ \tilde{\sigma} &= \left[\Gamma + \frac{\Gamma'}{\Gamma''}(1 - 2\Gamma') \right]^{1/2} \\ \psi &= \left[\frac{\Gamma - (q^*)^2}{2} \right]^{1/2} \\ \varphi &= \left[1 + \frac{\Gamma\left(\frac{2}{\Gamma''} - \Gamma\right)}{(\Gamma - (q^*)^2)^2} \right]^{1/2} \end{aligned} \quad (17)$$

In the above, ω , $\tilde{\sigma}$, ψ , and φ are all real; hence, it is a simple matter to extract the roots σ_1 and σ_2 from each case of eq 16. The expressions for q^* , Γ , Γ' , and Γ'' as functions of the reduced temperature $\tau = 1 - \chi/\chi_s$ and λ are given in Appendix A.

A plot of the normalized composition profile $m(z)/m_1$ according to eq 13 for various λ and at the reduced temperature $\tau = 0.1$ is given in Figure 1. The behavior of $m(z)$ for $\lambda > \lambda_L$ depends upon the value of the function ω in eqs 16 and 17, which in turn depends upon τ and λ . With the exception of a small region near $\lambda = 0$ and for τ near 1, one can show that, for $\lambda \geq 0$, ω is less than 1 for all τ . Thus, for blocky copolymers the profile is a monotonically decreasing function of z as it is for homopolymer blends.⁶ On the other hand, for $\lambda_L < \lambda < 0$ the profile $m(z)$ can be oscillatory or monotonic depending upon the temperature τ . Generally, the profile is oscillatory at large τ and becomes monotonic as τ decreases below some value $\tau^*(\lambda)$. Let $\kappa = \text{Im}(\sigma)$ denote the wavevector of the oscillation, where σ is given by eq 16. A plot of κ as a function of λ for various τ is given in Figure 2. As one can see, for $\lambda_L < \lambda < 0$, κ decreases smoothly to zero as $\tau \rightarrow 0$. This decrease of κ as $\tau \rightarrow 0$ has two causes. First, the homogeneous phase undergoes liquid-liquid phase separation as $\tau \rightarrow 0$ (for $\lambda > \lambda_L$). Thus, the melt will prefer to form a monotonic profile as it does for simple liquids. However, for $\lambda < 0$, there is a tendency for

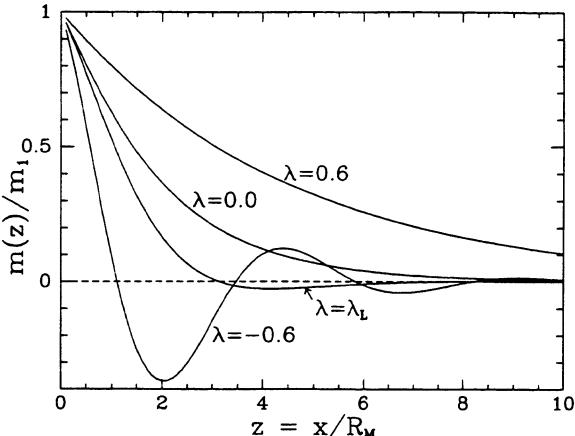


Figure 1. Normalized composition profile $m(z)/m_1$ ($m_1 = m(0)$) as a function of scaled distance $z = x/R_M$ for various λ according to eq 13. The reduced temperature $\tau = 1 - \chi/\chi_s(\lambda)$ is fixed at 0.1, and the value of λ corresponding to each profile is given in the figure.

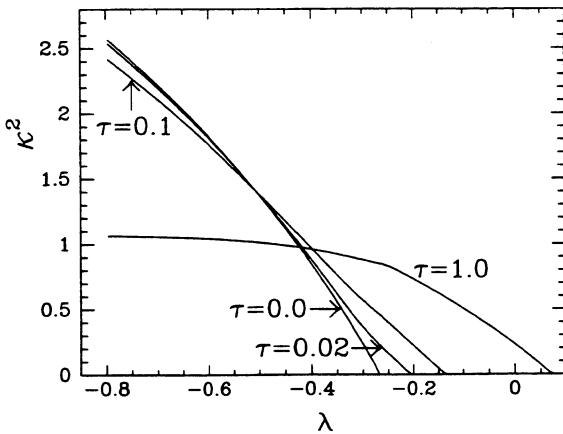


Figure 2. Wavevector κ of the oscillation of the composition profile $m(z)$ as a function of λ for various τ according to eq 17. τ for each curve is shown in the figure. Note that the $\tau = 0$ curve corresponds to $\kappa = q^*$, the minimum of $\Gamma(q)$.

alternating A-B regions on the chains with a characteristic (antiferromagnetic correlation) length l . Furthermore, the homogeneity of the melt is already broken by the presence of a surface excess m_1 . Hence, the profile will oscillate as long as the entropy penalty is not too large. Empirically, it appears that this oscillation will occur if the decay length ξ of the profile is not much larger than l . Also, since l increases as λ decreases, the tendency for oscillation will increase as λ becomes more negative. Lastly, the distribution in the size of the alternating regions is broad and continuous in the present case $|\lambda| \ll 1$, so $\kappa \rightarrow 0$ smoothly as ξ increases.

From the expressions for σ given in eq 16, one can see that, for chemical correlations such that $\lambda < \lambda_L$, σ is complex and therefore the composition profile will always oscillate. Furthermore, the wavevector κ of this oscillation is temperature dependent (see Figure 2), with $\kappa \rightarrow q^*$, the minimum of $\Gamma(q)$, as $\tau \rightarrow 0$. Given that for these copolymers there is a tendency for alternation of A and B segments on the chains, this behavior is consistent with that for diblock copolymers.¹⁰ Even more interestingly, κ can increase or decrease depending upon the value of λ . For $-1 < \lambda \leq -0.5$, κ increases as τ decreases. This behavior is opposite to that for the region $\lambda_L < \lambda < 0$. An explanation is that as $\tau \rightarrow 0$, and $\lambda < \lambda_L$, the melt undergoes a transition to a disordered microphase. The microphase is characterized by A-rich or B-rich regions with an inverse size k_0

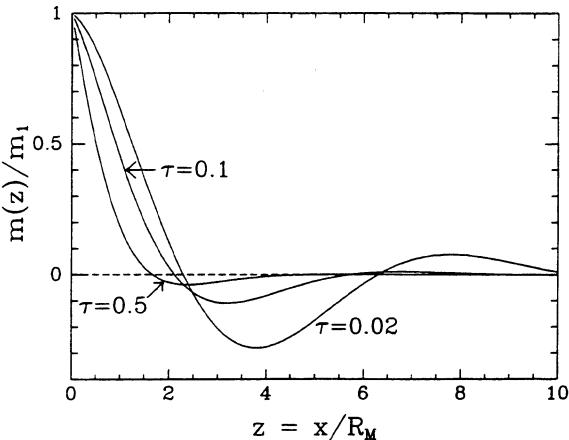


Figure 3. Normalized composition profile $m(z)/m_1$ as a function of the scaled distance $z = x/R_M$ for $\lambda = -0.35$ at various temperatures τ according to eq 13. The value of λ for each curve is shown in the figure.

that equals q^* at $\tau = 0$ and increases as the temperature is lowered.²⁰ Thus, for $\lambda \leq -0.5$, one sees a continuous increase in the oscillation period κ as χ increases to and past its spinodal value χ_s . However, for $-0.4 \leq \lambda \leq \lambda_L$, κ decreases as τ decreases in the same manner as for the region $\lambda_L < \lambda < 0$. A plot of $m(z)/m_1$ as a function of z for $\lambda = -0.35$ and at various τ is given in Figure 3. In contrast, for the small region $-0.5 \leq \lambda \leq -0.4$, κ first increases and then decreases as $\tau \rightarrow 0$. Thus, one sees a continuous change in the behavior of the profile $m(z)$ as λ increases from -1 to $+1$. Finally, we note that the length scale $\xi = Re(\sigma)$ of the decay of $m(z)$ has the usual mean-field dependence on temperature, $\xi \sim \tau^{-1/2}$, for all λ as $\tau \rightarrow 0$.

With $m(z)$ given by eqs 13–17, we can now determine the equilibrium value of the surface tension $\gamma[m]$. Using the Euler–Lagrange equation (eq 12), the equilibrium form of γ can be simplified to

$$\gamma = \gamma_0 + \frac{1}{v} f_s(m_1) + \frac{R_M m_1^2}{2v M f(1-f)} \tilde{K}^{-1}(\tau, \lambda) \quad (18)$$

where

$$\tilde{K}^{-1}(\tau, \lambda) = -cm'(0)/m_1 \quad (19)$$

Use of eq 13 yields

$$\tilde{K}(\tau, \lambda) = \frac{b^2 + \sigma_1 \sigma_2}{c \sigma_1 \sigma_2 (\sigma_2 + \sigma_1)} \quad (20)$$

Lastly, γ must be a minimum with respect to the surface composition m_1 .²⁸ This relation yields

$$m_1 = \frac{\bar{\mu}}{\left[\frac{R_M \tilde{K}^{-1}(\tau, \lambda)}{M f(1-f)} - g \right]} \quad (21)$$

Then, with eqs 18 and 21, the surface tension is

$$\gamma = \gamma_0 - \frac{1}{2v} \left[\frac{\bar{\mu}^2}{\frac{R_M}{M f(1-f) \tilde{K}(\tau, \lambda)} - g} \right] \quad (22)$$

This expression has essentially the same form as was found in our earlier work.²³ In the only experimental estimate of which we are aware, g is negative.²⁶ For simplicity, we consider cases where g , if positive, is small compared to $R_M/2Mf(1-f)\tilde{K}$. Then, the reduction in the surface

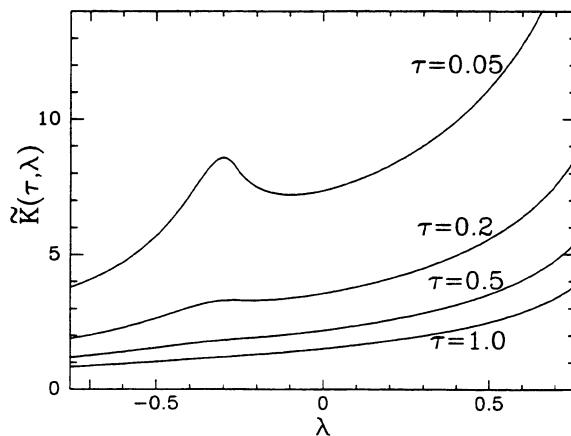


Figure 4. Dimensionless function $\tilde{K}(\tau, \lambda)$ as a function of λ for various reduced temperatures τ . The explicit expression for \tilde{K} is given by eq 20. The value of τ for each curve is given in the figure. The reduction in surface tension $\Delta\gamma$ is roughly proportional to \tilde{K} .

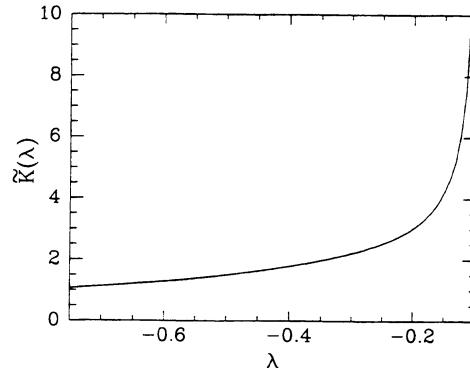


Figure 5. Dimensionless function \tilde{K} of λ at fixed x or absolute temperature T . The values of $2Mf(1-f)x$ have been set to equal to 1.16 so that $\tau = 0$ at $\lambda \sim 0.1$. Since $\tilde{K} \sim \tau^{-1/2}$ as $\tau \rightarrow 0$, \tilde{K} becomes infinite at this value of λ .

tension, $\Delta\gamma = \gamma_0 - \gamma$, due to the formation of a nonzero composition profile $m(z)$, is seen to increase with the block size M and increasing compositional symmetry of the copolymer. Further, with g small, $\Delta\gamma$ is roughly proportional to $\tilde{K}(\tau, \lambda)$. A graph of \tilde{K} as a function of λ for various τ is given in Figure 4. In conjunction with this plot, it can be seen that $\Delta\gamma$ is an increasing function of λ for fixed τ and is a decreasing function of τ for fixed λ . An exception to this behavior is that, for small τ , \tilde{K} develops a local maximum at $\lambda \approx \lambda_L$. This behavior is an artifact of making the comparison at fixed τ rather than for fixed temperature T or χ . τ decreases strongly with increasing λ for fixed χ and has an inflection near the Lifshitz point. If $\Delta\gamma$ is examined as a function of λ at fixed x rather than τ , as is done in Figure 5, one finds that $\Delta\gamma$ increases monotonically with λ . Thus, we find that blocky copolymers have a lower surface tension than ideal copolymers, and ideal copolymers a lower one than alternating copolymers, all other features of the copolymers being equal.

The finding that increases in M or λ lead to a reduction in surface tension can be understood in the context of the balance of entropic and energetic factors that establish a nonvanishing surface composition profile. Copolymers with large values of M and λ have long correlated sequences of consecutive A monomers or consecutive B monomers along their backbones. The entropy penalty that such chains must pay in order to place a given amount of A monomers at the surface is considerably less than the penalty suffered by copolymers whose A and B monomers are intimately “mixed” along the backbones. Hence, when

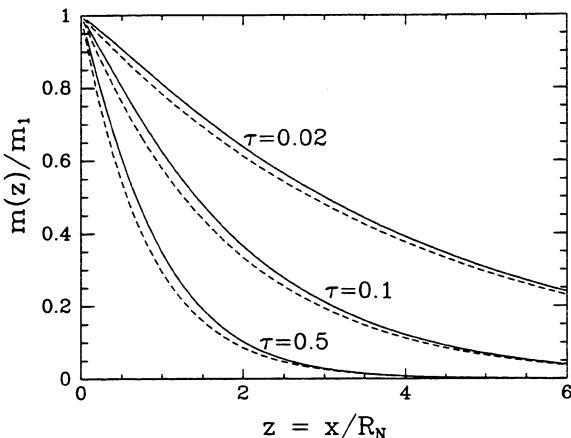


Figure 6. Normalized composition profile $m(z)/m_1$ for homopolymer blends as a function of the scaled distance $z = x/R_N$ for various temperatures τ . The value of τ for each curve is given in the figure. The solid lines correspond to results for the theory here, and the dashed lines correspond to making a "square-gradient" approximation, given by eq 23, to $1/G_2(q)$.

compared at the same value of the surface field $\tilde{\mu}$, blocky copolymer melts will have a lower surface tension.

III. Homopolymer Blends and Diblock Copolymers

Given the above results for random multiblocks, it is interesting to examine the surface behaviors of the limiting cases of homopolymer blends and diblock copolymers and compare them with results from previous investigations. Note that, with straightforward changes in the values of the parameters, the form of $F_b[m]$ given by eq 7 can be used to describe the bulk free energy, to quadratic order in $m(z)$, of blends or diblocks. Thus, it is a relatively simple matter to modify the above theory to describe these systems.

A. Homopolymer Blends. Setting $\lambda = 0$ and $M \rightarrow N$ ($R_M \rightarrow R_N$), $F_b[m]$ given by eqs 4 and 5 becomes the bulk free energy of a homopolymer blend with $\bar{a}_A = \bar{a}_B$.⁴ In previous investigations of blends at surfaces,⁶ $G_2(q)$ in eq 5 (and given explicitly by eq A.1) is approximated by a square-gradient expansion

$$\frac{1}{G_2(q)} \approx \frac{1}{Nf(1-f)} \left(1 + \frac{1}{3}q^2\right) \quad (23)$$

This form is weakly nonlocal; that is, the interactions are short-ranged on the scale of R_N . However, in the present work, the surface potential $e^{-b(z_1+z_2)}$ arose only because our approximation to $1/G_2(q)$ (eq 6) produced a term that was strongly nonlocal $\sim e^{-b|z_1-z_2|}$. Thus, if the square-gradient expansion is a good approximation to $1/G_2(q)$, previous workers on blends near surfaces are justified in ignoring restrictions on chain conformations of the type described in this work. The square-gradient approximation to $1/G_2$ can be shown to be accurate to within 30% for all wavevectors $q = kR_N$. On the other hand, the form for $\Gamma(q)$, given by eq 6, with the fitting scheme described in Appendix A, yields an approximation to $1/G_2$ that is accurate to 3% for all q . We have investigated how this improved approximation changes the profile $m(z)$. A plot of $m(z)/m_1$ as a function of z for various τ using both approximations is given in Figure 6. With one exception, it can be seen that the difference between the two approximations for $1/G_2$ produces only a small quantitative change in the surface profiles. The exception is that, at small τ ($\tau = 0.02$ in Figure 6), the present theory yields a flatter profile at short distances ($z \leq 0.5$) than the square-

gradient theory. However, this difference is small. Thus, it is unclear to us at this time whether making better approximations to the vertex functions, e.g., $\Gamma_{2(q)} \sim 1/G_2(q)$, in the bulk free energy and restricting chain conformations at the surface will account for the discrepancy between the Schmidt-Binder theory⁶ and the experimental results of Jones et al.^{26,29} for the surface profile of an isotopic homopolymer blend.

B. Diblock Copolymers. Our approximate form for $\Gamma(q)$, given by eq 6, is identical to approximations used in previous work^{10,30,31} on diblocks if one lets $M \rightarrow N$, $b^2 = 0$, $a = 3/2f(1-f)$, $c = 1/2$, and $d = -\chi f(1-f)$. Here $\chi = 2(\chi N - \chi_s N) + 3^{1/2}[1/f(1-f)]^{3/2}$, where χ_s is the spinodal value of χ . Indeed, to quadratic order in $m(x)$, the free energy for alternating multiblocks ($\lambda = -1$) is qualitatively the same as that for diblocks.

A previous study of the properties of diblocks near surfaces that also employs the RPA approach to polymer melts^{4,25} has been carried out by Fredrickson.¹⁰ Except for the additional surface term, $F_s^S[m]$, our form for $\gamma[m]$ (eq 3) is identical to his. In addition, the effect of the surface term is greatest for alternating multiblocks and diblocks since the range l of the surface potential is infinite. However, Fredrickson imposed an additional constraint on the profile $m(z)$ which, for the special case of diblocks, is equivalent to including the extra term F_s^S . To explain this result, we note that for perfectly alternating multiblocks or diblocks all chains are identical (neglecting polydispersity). Thus, the composition $m(x)$, averaged over a volume which greatly exceeds the chain volume R_N^3 , must be zero for all portions of the melt. In the present case, this constraint takes the form

$$\int_0^h dz m(z) = 0 \quad (24)$$

where $h \gg \xi$ and ξ is the decay length of the profile. It can be shown that the expression for $m(z)$ (eq 13) satisfies this constraint when $b^2 = 0$, i.e., for alternating multiblocks or diblocks. Hence, the results of the theory for the profile $m(z)/m_1$ are consistent with Fredrickson's results for monodisperse diblock copolymers. Qualitatively and quantitatively similar profiles have been obtained by numerical self-consistent-field methods by Shull.³²

IV. Discussion

In the present paper we have analyzed the surface ordering and interfacial tension of a simple model of random block copolymer melts. While highly idealized, the model and analysis provide valuable insight into the equilibrium surface properties of commercial or laboratory heterogeneous polymers. Although it is generally the case that one component of a heteropolymer is energetically favored at a surface, any surface excess that develops is associated with a translational and conformational entropy cost. In the present paper we have shown that this entropy cost can be quantified and proves to be a sensitive function of both the composition and the sequence distribution of the copolymer. As a consequence, it follows that the interfacial profile and surface tension are strongly dependent on these same parameters. A particularly striking result is that this entropy cost (and hence surface tension) is smallest for copolymers with long blocks of species A or B and largest for alternating copolymers of the same composition and molecular weight. This suggests that one can fine-tune the interfacial properties of heteropolymers by controlling their sequence distributions.

In the present model of random block copolymers, which is the same as that employed by Fredrickson, Milner, and Leibler (FML), the sequence distribution can be contin-

uously tuned from perfectly alternating to completely blocky (A and B homopolymers) by varying a single parameter λ from -1 to +1. With the assumption that the bulk material is homogeneous and that the compositional inhomogeneities induced by the surface are weak, we have derived explicit analytical expressions for the composition profile (eq 13), the surface composition, (eq 21), and the surface tension (eq 22) as functions of λ , the average composition, f , the segment degree of polymerization, M , and the reduced temperature, τ . Due to the presence of an isotropic Lifshitz point in the model at $\lambda = -0.268$, the composition profile induced by a surface can either decay monotonically or in a damped oscillatory fashion. Hence, the locus of surface behaviors generated by the family of copolymers characterized by different values of λ encompasses both the usual surface enrichment encountered in polymer blends and the oscillatory profiles observed at diblock copolymer interfaces.

Some of the assumptions made in the analysis of this paper need to be considered when applying the results to experimental measurements or for the purpose of extrapolating such measurements. In particular, the assumption of weak compositional inhomogeneities can be verified by means of a surface profiling technique such as SIMS or neutron reflectivity. However, Shull³² has shown that, for diblock copolymers, a theory similar to that described here¹⁰ is capable of reproducing the full mean-field composition profile in situations where the inhomogeneities are substantial. Hence, we might hope that the present theory would be quantitative in this regard even outside the region of its strict applicability. Another concern is the neglect of long-ranged interactions, such as electrostatic or van der Waals, in the phenomenological expression used for F_s^E (eq 8). Previous workers have discussed the relevance of such interactions⁷ to surface enrichment and wetting phenomena in blends, and they will undoubtedly play a role under some conditions at heteropolymer surfaces. We have neglected such interactions in the present analysis for the sake of simplicity, but they could be easily added to eq 8 if deemed necessary to render the theory quantitative. It should also be pointed out that the applicability of the present theory to crystallizable block copolymers at surfaces is further limited to temperatures above the melting point of the crystallizable block. In conjunction with this limitation, we note that Stafatos et al. have predicted a freezing transition for a collapsed ideal random copolymer chain which, in some cases, prevents the existence of a disordered microphase within the globule.³³ As the configurational entropy of a chain in a melt is much larger than when it is in a collapsed state, we do not believe that such a situation will occur for the type of system considered here or in the original work of FML. However, the question remains open, and thus Stafatos et al.'s prediction should be kept in mind when applying the predictions of FML or the present theory to real copolymer melts. Finally, we note that the validity of the mean-field assumption breaks down in the extreme vicinity of the microphase or liquid-liquid spinodal and fluctuation effects must be considered.

Extensions of the present model and analysis to remedy the above shortcomings are fairly straightforward yet may depend in some detail on the chemical nature of the heteropolymer of interest. Another obvious extension would be to investigate the rich variety of wetting phenomena that are possible in microphase-separated, random copolymeric materials. We intend to pursue this and related problems in the near future but look for guidance from the experimental community in the form

of surface tension and profile measurements on well-characterized heteropolymer melts.

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Appendix A

In this appendix we construct an approximant to the two-point vertex function $\Gamma_2(q, k) = [G_2^{-1}(q) - 2\chi]\delta(q+k)$ used in the FML theory. In the limit $|\lambda|^Q \ll 1$, FML find that the noninteracting two-point Green's function $G_2(q)$ is given by the expression:

$$G_2(q, \lambda) = Mf(1-f) \left[g(x) + \frac{2\lambda h(x)}{1-\lambda \exp(-x)} \right] \quad (\text{A.1})$$

Here, $x = q^2 R_M^2$, $g(x)$ is the Debye function,

$$g(x) = \frac{2}{x^2} [x - 1 + \exp(-x)] \quad (\text{A.2})$$

and

$$h(x) = \left(\frac{1 - \exp(-x)}{x} \right)^2 \quad (\text{A.3})$$

In what follows, we will express all wavevectors in terms of R_M^{-1} .

Next, we define a function $\Gamma(q)$ by

$$\Gamma_2(q, k) = \frac{1}{Mf(1-f)} \Gamma(q) \delta(q+k) \quad (\text{A.4})$$

An approximate representation of $\Gamma(q)$ that we have found most convenient is

$$\Gamma(q) \simeq \Gamma_A(q) = \frac{a}{q^2 + b^2} + cq^2 + d \quad (\text{A.5})$$

Our reasoning for this form is as follows. In the blocky limit, $\lambda \rightarrow +1$, but $|\lambda|^Q \ll 1$, an expansion of $\Gamma(q)$ about $q = 0$ to first order in q^2 is very accurate for all wavevectors. In the opposite, alternating coblock limit, $\lambda = -1$, $\Gamma(q) \sim 1/q^2$ as $q^2 \rightarrow 0$, and $\Gamma(q) \sim q^2$ for $q^2 \gg 1$. This behavior can be recovered from eq A.5 by setting $b^2 = 0$. Thus, with a , b , c , and d as functions of λ , the above form for Γ is expected to interpolate smoothly between these various limits of λ and q .

Our past experience with block copolymers at surfaces¹⁰ leads us to expect the interface profile to be dominated by those wavevectors near the wavevector that minimizes Γ , q^* . Thus, our scheme is to require that the parameters a , b , and d be determined by requiring that eq A.5 yield the exact values for $\Gamma(q^*)$, $\Gamma'(q^*)$, $\Gamma''(q^*)$, where $\Gamma^{(n)}(q^*) = (d^n/dq^{2n})\Gamma|_{q^*}$. Lastly, c is determined by requiring that eq A.5 yield the correct asymptotic behavior of Γ for $q \gg 1$. This last relation gives

$$c = 1/2 \quad (\text{A.6})$$

Solving for a , b , and d in terms of Γ , Γ' , Γ'' , and q^* , we find

$$\begin{aligned} a &= \frac{(1 - 2\Gamma')^3}{2(\Gamma'')^2} \\ b &= \frac{1 - 2\Gamma'}{\Gamma''} - (q^*)^2 \\ d &= \Gamma - \frac{1}{2} \left(\frac{(1 - 2\Gamma')^2}{\Gamma''} + (q^*)^2 \right) \end{aligned} \quad (\text{A.7})$$

Here,

$$\Gamma(q^*) = \tau Mf(1-f) G_2^{-1}(q^*, \lambda) \quad (\text{A.8})$$

where

$$\tau = 1 - \chi/\chi_s \quad (\text{A.9})$$

The reduced temperature τ is proportional to the difference of χ from its spinodal (liquid-liquid separation for $\lambda > \lambda_L$) and microphase separation for $\lambda < \lambda_L$) value $\chi_s = (1/2)G_2^{-1}(q^*, \lambda)$.

The remaining factor in eq A.8 can be parametrized as

$$Mf(1-f)G_2^{-1}(q^*) =$$

$$\begin{cases} \frac{1-\lambda}{1+\lambda}, & \lambda \geq \lambda_L \\ 0.793 - 3.765\lambda - 0.789\lambda^2, & \lambda \leq \lambda_L \end{cases} \quad (\text{A.10})$$

Note that this factor is a function solely of λ and thus the M , f , and T dependence of $\Gamma(q)$ enters only through τ . Similarly, the λ -dependent coefficients appearing in eq A.7 are given by

$$\Gamma'(q^*) = \begin{cases} \frac{1+4\lambda+\lambda^2}{3(1+\lambda)^2}, & \lambda \geq \lambda_L \\ 0, & \lambda \leq \lambda_L \end{cases} \quad (\text{A.11})$$

$$\Gamma''(q^*) = \begin{cases} \frac{1}{18}(1-\lambda)^3, & \lambda \geq \lambda_L \\ 0.223 - 0.329\lambda - 0.202\lambda^2, & \lambda \leq \lambda_L \end{cases} \quad (\text{A.12})$$

$$(q^*) = \begin{cases} 0, & \lambda \geq \lambda_L \\ -2.295 - 10.485\lambda - 7.663\lambda^2 - 2.715\lambda^3, & \lambda \leq \lambda_L \end{cases} \quad (\text{A.13})$$

The expressions for $\lambda \leq \lambda_L$ are numerical fits to the exact results. All are accurate to within 3%.

Within the above fitting scheme, the approximant $\Gamma_A(q)$ is accurate to within 10% for all q and for $-0.7 \leq \lambda < 1$. The scheme breaks down for $\lambda < -0.85$ as b^2 becomes negative. However, our primary interest here is for experimentally relevant values of λ not too close to +1 or -1, and so we will ignore this problem.

Appendix B

In this appendix we outline the derivation of a Landau expansion of the free energy $F[m]$ for a random multiblock copolymer melt in the presence of a neutral impenetrable planar surface. We assume that there are no energetic interactions between the surface and the melt; thus, the only effect of the surface is to prevent chains from crossing the plane $z = 0$. As in FML, the melt consists of linear A-B multiblock copolymers, with each chain made up of a stochastic sequence of segments A_M and B_M , each with M monomers, for a total of Q ($>> 1$) segments per chain. The fundamental variables of our microscopic theory are the set of monomer positions $\{\mathbf{R}_i(s)\}$, where $i = 1, 2, \dots, N_p$ indexes of the various chains and $s = 1, 2, \dots, N$ ($= MQ$) indexes of the monomers along a chain. In addition, we associate with monomer s on chain i on occupation variable σ_{il} , where $l = l(s) = \text{int}(s/M) + 1$ indexes the subblocks (segments) on the chain. σ_{il} has a zero mean and takes the value $2(1-f)$ or $-2f$ if the monomer belongs to a type-A or type-B segment, respectively. In the following, it will be convenient to scale all lengths in terms of the segment radius of gyration R_M , and all energies in terms of $k_B T$.

The starting point of this derivation is the partition function Z in the canonical ensemble. Z is given by eq B.1 in FML. Z is obtained by averaging over the set of microscopic positions $\{\mathbf{R}_i(s)\}$, while enforcing incompress-

ability. Following FML, we find

$$Z = \int D[m] D[J] e^{(\chi/\tilde{v}) \int d\mathbf{x} m^2(\mathbf{x})} e^{-W[m, J]} \quad (\text{B.1})$$

which is similar to eq B.6 of FML. Here, $m(\mathbf{x}) = \phi_A(\mathbf{x}) - f$ is a concentration order parameter where $\phi_A(\mathbf{x})$ is the volume fraction of type-A monomers at the point \mathbf{x} . $J(\mathbf{x})$ is a dummy chemical potential field, and $D[m]$ and $D[J]$ denote a sum over the space of fields for m and J , respectively. The parameter \tilde{v} is defined by $\tilde{v} = v/R_M^3$, where v is the monomer volume. The term $(\chi/\tilde{v}) \int d\mathbf{x} m^2(\mathbf{x})$ describes the energetic preference of like monomer contacts over dissimilar monomer contacts; χ is the usual Flory parameter. Finally, the functional $W[m, J]$ is given by

$$W[m, J] = -i \int d\mathbf{x} J(\mathbf{x}) m(\mathbf{x}) + \frac{N_p(\tilde{v})^2}{8} \sum_{s,s'} \langle \sigma_s \sigma_{s'} \rangle_\sigma \langle J(\mathbf{R}(s)) J(\mathbf{R}(s')) \rangle_0 \quad (\text{B.2})$$

In $W[m, J]$, we have retained terms only to quadratic order in the field $J(\mathbf{x})$. $\mathbf{R}(s)$ and $\mathbf{R}(s')$ denote monomer positions on the same chain. The bracket $\langle \dots \rangle_0$ denotes an average with respect to the variables $\{\mathbf{R}_i(s)\}$ with statistical weight $e^{-H_0(\mathbf{R}_i(s))}$, where $H_0(\mathbf{R}_i(s)) = [3/2(\tilde{a})^2] \sum_{i,s} (\mathbf{R}_i(s) - \mathbf{R}_i(s+1))^2$ is the Edwards' Hamiltonian. Here, $\tilde{a} = \bar{a}_{AB}/R_M$, where \bar{a}_{AB} is the statistical segment length. Finally, $\langle \dots \rangle_\sigma$ denotes an average with respect to the set of occupation variables $\{\sigma_{il}\}$.

Next, we need to perform the integration over the field J to obtain the mean-field free energy $F[m]$. This calculation is simplified by assuming that the melt occupies the space $-\tilde{L} \leq z \leq \tilde{L}$, where $\tilde{L} = L/R_M$. Without loss of generality, we can restrict the fields $m(\mathbf{x})$ and $J(\mathbf{x})$ to those which are symmetric about the plane $z = 0$. Then, half the chains occupy the space $z > 0$ and the other half the space $z < 0$. That is, the plane $z = 0$ acts as an infinitely thin wall dividing the melt in half and reflects chain configurations so that there is no interaction between the halves. Lastly, the thickness L of a half-slab is assumed to be much larger than any other relevant length scale and so can be treated as effectively infinite in the following. With this geometry we can use and exploit the properties of exponential Fourier transforms.

As we will be restricting our attention to one-dimensional profiles $m(\mathbf{x}) = m(z)$, we can restrict the field J to be one-dimensional also. Next, we define the Fourier transform pair

$$m(z) = \int_k e^{ikz} m(k) \\ m(k) = \int_{-L}^L dz e^{-ikz} m(z) \quad (\text{B.3})$$

and likewise for $J(z)$ and $J(k)$. Here, $\int_k = (1/2\tilde{L}) \sum_k \simeq \int_{-\Lambda}^{\Lambda} dk / 2\pi$, where the \sum_k denotes a sum over all reciprocal wavevectors k . Λ is an ultraviolet cutoff and is expected to scale as $1/\tilde{v}^{1/3}$. In what follows, Λ will be treated as infinite unless explicitly stated otherwise. Expressed in terms of the Fourier components of the fields, $W[m, J]$ has the form

$$W[m, J] = -i \tilde{S} \int_k J(k) m(-k) + \frac{N_p(\tilde{v})^2}{4} \int_{k,q} J(k) J(q) G(k, q) \quad (\text{B.4})$$

Here, $\tilde{S} = S/R_M^2$ is the area of the plane $z = 0$, and

$$G(k,q) = \frac{1}{2N} \sum_{s,s'} \langle \sigma_s \sigma_{s'} \rangle_\sigma \langle e^{ikz(s)} e^{iqz'(s')} \rangle_0 \quad (\text{B.5})$$

with $z(s)$ denoting the coordinate of the monomer position $\mathbf{R}(s)$ perpendicular to the plane $z = 0$. The average $\langle \dots \rangle_0$ is different for chains on different sides of the plane $z = 0$ but has the same value for chains on the same side of the plane. Thus, one can write

$$G(k,q) = G^r(k,q) + G^l(k,q) \quad (\text{B.6})$$

where

$$G^r(k,q) = \frac{1}{4N} \sum_{s,s'} \langle \sigma_s \sigma_{s'} \rangle_\sigma \langle e^{ikz(s)} e^{iqz'(s')} \rangle_0^r \quad (\text{B.7})$$

and the average $\langle \dots \rangle_0^r$ is taken over the half-space $z > 0$ with the appropriate (reflecting) boundary condition at $z = 0$. Likewise, $G^l(k,q)$ is the same as G^r except for the replacement of the average $\langle \dots \rangle_0^r \rightarrow \langle \dots \rangle_0^l$, where $\langle \dots \rangle_0^l$ is appropriate for chains occupying the space $z < 0$.

Next, we need to determine the averages $\langle \dots \rangle_0^r$ and $\langle \dots \rangle_0^l$. As Edwards has shown, all averages with respect to the Hamiltonian \mathcal{H}_0 can be computed using products of a Green's function $G_E(\mathbf{r},s;\mathbf{r}',s')$. Here, $G_E(\mathbf{r},s;\mathbf{r}',s')$ is related to the conditional probability that monomer s' is at position \mathbf{r}' if monomer s is at position \mathbf{r} .³⁴ For the average $\langle \dots \rangle_0^r$, the appropriate conditions on G_E , denoted by G_E^r , are (1) G_E^r obeys the free diffusion equation for $z \geq 0$ as chains are ideal in a melt in the absence of A-B interactions, (2) $G_E^r = 0$ for $z < 0$, and (3) $\partial G_E^r / \partial z|_{z=0^+} = \partial G_E^r / \partial z'|_{z=0^+} = 0$. The no-flux boundary condition arises because we are considering an incompressible melt. Thus, we require that the density be spatially uniform, i.e., that $\langle \rho_i(\mathbf{x}) \rangle_0 = \text{constant}$, where $\rho_i(\mathbf{x}) = \sum_s \delta(\mathbf{x} - \mathbf{R}_i(s))$ is the contribution to the density from the i th chain. With these conditions, one finds, after integrating over the coordinates parallel to the plane $z = 0$, that

$$G_E^r(z,s;z',s') = \frac{1}{\pi^{1/2} 2D} [\exp(-(z-z')^2/4D^2) + \exp(-(z+z')^2/4D^2)] \Theta(z) \Theta(z') \quad (\text{B.8})$$

Here, $D^2 = |s - s'| \bar{a}^2/6$, where $\bar{a} = \bar{a}_{AB}/R_M$ and \bar{a}_{AB} is the statistical segment length. $\Theta(z)$ is the Heaviside step ("theta") function with $\Theta = 1$ for $z > 0$ and $\Theta = 0$ for $z < 0$.

With this Green's function we have

$$\langle e^{ikz(s)} e^{iqz'(s')} \rangle_0^r = \frac{1}{L} \int_{-\infty}^{+\infty} dz dz' G_E^r(z,s;z',s') e^{ikz} e^{iqz'} \quad (\text{B.9})$$

It is convenient here to use the integral form of $\Theta(z)$:

$$\Theta(z) = \int_{-\infty}^{+\infty} \frac{dw}{2\pi i} \frac{e^{iwz}}{w - i\delta} \quad (\text{B.10})$$

with $\delta = 0^+$. We then find, after some calculation, that

$$G^r(k,q) = \frac{1}{L} \int_{-\infty}^{+\infty} \frac{dy}{2\pi} \frac{1}{y - k - i\delta} \left[\frac{1}{y + q + i\delta} - \frac{1}{y - q - i\delta} \right] G_2(y) \quad (\text{B.11})$$

Here, $G_2(q)$ is the noninteracting two-point correlation function for an infinite system

$$G_2(q) = \frac{1}{4N} \sum_{s,s'} \langle \sigma_s \sigma_{s'} \rangle_\sigma \exp(-q^2 |s - s'| \bar{a}^2/6) \quad (\text{B.12})$$

and is equivalent to eq A.1 for $|\lambda|^Q \ll 1$. To perform the integration over the dummy variable y , we make use of

the approximant for $\Gamma_2(q,k)$, given in Appendix A. Then,

$$G_2(q) \simeq Mf(1-f)\Gamma_{A1}^{-1}(q) \quad (\text{B.13})$$

where $\Gamma_{A1}(q)$ is the value of $\Gamma_A(q)$ for $\tau = 1$.

Let $\pm i\tilde{\sigma}_1$ and $\pm i\tilde{\sigma}_2$ be the four zeros of $\Gamma_{A1}(q)$, and thus $\tilde{\sigma}_1$ and $\tilde{\sigma}_2$ satisfy eq 15 for $\tau = 1$. Then, Γ_{A1}^{-1} can be written as

$$\Gamma_{A1}^{-1}(q) = \frac{1}{c} \frac{q^2 + b^2}{(q^2 + \tilde{\sigma}_1^2)(q^2 + \tilde{\sigma}_2^2)} \quad (\text{B.14})$$

The quantities $\tilde{\sigma}_1$ and $\tilde{\sigma}_2$ can be real or complex depending upon the value of λ . However, since our final result for $F[m]$ does not depend explicitly on $\tilde{\sigma}_1$ or $\tilde{\sigma}_2$, we will perform the integration of eq B.11 only for $\lambda < \lambda_L$. For $\lambda < \lambda_L$, from eq 15, one finds $\tilde{\sigma}_1 = \alpha - i\beta$ and $\tilde{\sigma}_2 = \tilde{\sigma}_1^*$, where α and β are real, positive, and nonzero constants, and the asterisk denotes complex conjugation. Performing the integral over y , we find

$$G^r(k,q) = \frac{Mf(1-f)}{L} \left[\frac{i}{q + k + 2i\delta} \Gamma_{A1}^{-1}(q) - \frac{2q}{(q^2 + \tilde{\sigma}_1^2)} \frac{h_1}{k + i\tilde{\sigma}_1} - \frac{2q}{(q^2 + \tilde{\sigma}_2^2)} \frac{h_2}{k + i\tilde{\sigma}_2} \right] \quad (\text{B.15})$$

with

$$h_1 = \frac{1}{2c} \frac{b^2 - \tilde{\sigma}_1^2}{\tilde{\sigma}_1(\tilde{\sigma}_1^2 - \tilde{\sigma}_2^2)} \quad (\text{B.16})$$

and $h_2 = h_1(1 \leftrightarrow 2)$. Thus, with $G^l(k,q) = G^r(k,q)^*$, our final form for $G(k,q)$ is

$$G(k,q) = \frac{Mf(1-f)}{L} \left[\delta(q+k) \Gamma_{A1}^{-1}(q) - \sum_{i=1}^2 f_i(k) f_i(q) \right] \quad (\text{B.17})$$

where

$$f_1(k) = (4h_1)^{1/2} \frac{k}{k^2 + \tilde{\sigma}_1^2} \quad (\text{B.18})$$

and $f_2 = f_1(1 \leftrightarrow 2)$. Here, we have used the relation $2\epsilon/(q^2 + \epsilon^2) = \delta(q)$, where $\delta(q)$ is the one-dimensional Dirac delta function.

Now, let us return to the integral over $[J]$,

$$\int D[J] e^{-W[m,J]} \quad (\text{B.19})$$

This integral is performed by determining the saddle-point Fourier coefficient $\tilde{J}(q)$. $\tilde{J}(q)$ satisfies $\delta W/\delta J(q)|_{J(q)} = 0$, which, with eq B.4, gives

$$-i\tilde{S}m(-q) + \frac{N_p N \tilde{v}^2}{2} \int_k \tilde{J}(k) G(k,q) = 0 \quad (\text{B.20})$$

Although the last terms in eq B.17 for $G(k,q)$ are not diagonal, they are separable. Hence, the solution of $\tilde{J}(k)$ can be determined exactly.³⁵ We find

$$\tilde{J}(q) = \tilde{m}(q) \Gamma_{A1}(q) + \sum_{i=1}^2 \Gamma_{A1}(q) A_i f_i(-q) \quad (\text{B.21})$$

with $\tilde{m}(q) = im(q)/\tilde{v}Mf(1-f)$, and we have used the relation $N_p N \tilde{v} = 2\tilde{S}\tilde{L}$. The coefficients A_i are given by

$$A_i = \sum_j \Omega_{ij} B_j \quad (\text{B.22})$$

with

$$B_j = \int_k \tilde{m}(k) \Gamma_{A1}(k) f_i(k) \quad (B.23)$$

Ω is a 2×2 matrix with an inverse $\Omega^{-1} = I - \Delta$. Here, I is the identity matrix, and Δ is a 2×2 matrix with components

$$\Delta_{ij} = \int_k \Gamma_{A1}(k) f_i(k) f_j(-k) \quad (B.24)$$

Upon expanding $J(k)$ in $W[m, J]$ about $\tilde{J}(k)$, eq. B.19 becomes

$$e^{-W[m, \tilde{J}]} \times \text{constant} \quad (B.25)$$

where

$$W[m, \tilde{J}] = -\frac{\tilde{S}\tilde{v}Mf(1-f)}{2} \left[\int_k \tilde{m}(k) \tilde{m}(-k) \Gamma_{A1}(k) + \sum_{ij} \Omega_{ij} B_i B_j \right] \quad (B.26)$$

In the determination of Ω , there arise terms that scale as $\int_k \sim \Lambda$, where Λ is an ultraviolet cutoff. These terms are dominant and, indeed, singular for $\Lambda \rightarrow \infty$, and hence all other terms of lower order in Λ can be dropped. However, it turns out that the Λ dependence of the coefficients in Ω cancels out. After some calculation (retaining only the most singular terms), we find

$$W[m, \tilde{J}] = \frac{\tilde{S}}{2\tilde{v}Mf(1-f)} \int_{k,q} m(q) m(k) \left\{ \Gamma_{A1}(q) \delta(k+q) - \frac{2a}{b} \frac{k}{k^2 + b^2} \frac{q}{q^2 + b^2} \right\} \quad (B.27)$$

Here, we have used the relation $a/c = (\tilde{\sigma}_1^2 - b^2)(\tilde{\sigma}_2^2 - b^2)$, which can be deduced from eq 15. Noting that $\Gamma_A(q) = \Gamma_{A1}(q) - 2Mf(1-f)\chi$ and combining eqs B.1, B.25, and B.27, the final form of the partition function is

$$Z = \int D[m] e^{-H[m]} \quad (B.28)$$

where the effective Hamiltonian is given by

$$H[m] = \frac{\tilde{S}}{2\tilde{v}Mf(1-f)} \int_{k,q} m(k) m(q) \left\{ \Gamma_A(q) \delta(k+q) - \frac{2a}{b} \frac{k}{k^2 + b^2} \frac{q}{q^2 + b^2} \right\} \quad (B.29)$$

In mean-field theory, $H[m]$ is identified as a free-energy functional; thus, $F[m] = H[m]$. Inverse Fourier transforming eq B.29 and specializing to the case of a half-

infinite slab with $m(z) = 0$ for $z < 0$, we arrive at the form of $F[m]$ given by the sum of eqs 7 and 10.

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