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Surface Ordering Phenomena in Block Copolymer Melts

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ABSTRACT: A mean field theory is presented to describe surface ordering phenomena in diblock copolymers near the microphase separation transition (MST). We consider a near-symmetric diblock melt in the vicinity of a solid wall or free surface, such as a film–air interface. The surface is allowed to modify the Flory interaction parameter and the chemical potential in the adjacent copolymer layer. The composition profile normal to the surface is investigated both above and below the MST. In contrast to the surface critical behavior of binary fluids or polymer blends, we find interesting oscillatory profiles in copolymers that arise from the connectivity of the blocks. These composition profiles might be amenable to study by ellipsometry, by evanescent wave-induced fluorescence, or by scattering techniques. Wetting and other surface phenomena and transitions in block copolymers are briefly discussed.

1. Introduction

Block copolymers constitute one of the most interesting classes of synthetic high-polymer materials and have great potential for specialty and high-technology applications. An important factor that contributes to the utility of block copolymers is that their macroscopic properties can be carefully tailored during synthesis by controlling molecular weight and composition. For a good introduction to the static and dynamic properties of block copolymers as well as their applications, we refer the interested reader to ref 1 and 2.

The vast majority of both experimental[1-8] and theoretical[9-18] investigations of molten block copolymers have dealt with the bulk properties of these materials. Much of this work has focused on the microphase separation transition (MST), at which a block copolymer forms spatially periodic ordered microphases. Starting with a disordered block copolymer, the MST can be approached either by lowering temperature or by stripping off a low molecular weight solvent that has been added to the copolymer melt to enhance miscibility and lower viscosity. The type of ordered morphology that forms at the MST depends on the composition and molecular architecture of the copolymer, but frequently encountered morphologies include one-dimensional lamellae, hexagonal packings of cylinders, and body-centered-cubic (BCC) arrays of spheres.

The theories for the equilibrium properties of block copolymers can be divided into two classes. The first class, the weak segregation limit theories,[10,14,17] are believed to be applicable to the disordered phase of copolymers and to the ordered microphases at temperatures very near the MST. They assume low amplitude composition patterns with no sharp interfaces between microdomains. Such theories make predictions for the location of the MST (in the parameter space of temperature, molecular weight, and composition) and for radiation scattering in the disordered phase. These predictions are in reasonable qualitative agreement with experiment, although some quantitative discrepancies have been found.[3,7] The second class of theories is the strong segregation limit theories,[9,11-13] which are applicable to well-developed ordered microdomains. These theories are believed to be most accurate at low temperature when the widths of the interfaces between microdomains are narrow relative to the size of a domain. The strong segregation theories are also in reasonable agreement with experiment.[3,6,7]

Recently, kinetic theories have been developed to describe the low-frequency dynamics of block copolymers in the vicinity of the MST.[15,16,18,36] These theories are dynamical extensions of the weak segregation limit equilibrium theories discussed above. They make predictions for the radiation scattering from diblocks under steady flow fields,[15] for the linear viscoelastic properties of disordered melts near the MST,[16,36] and for the early stages of the ordering dynamics following a quench across the MST.[18] Unfortunately, there has been much less experimental work on the dynamics of block copolymers, so few of these predictions have been tested in the laboratory.

All of the above-mentioned theories and experiments have focused on the *bulk* static or dynamic properties of block copolymers, i.e., the macroscopic and fluctuation properties far from any bounding surfaces or interfaces. In contrast, there have been only a handful of experimental studies on the behavior of block copolymers near surfaces.[19-21] Furthermore, we are not aware of any theoretical work on the equilibrium or kinetic surface properties of molten block copolymers. Because block copolymers are finding increasing applications as thin films, adhesives, and surfactants, it would seem that a fundamental understanding of their surface phenomena is essential.

The present paper is a contribution to the equilibrium theory of block copolymers near a surface. For simplicity we consider a diblock copolymer melt that orders into the lamellar morphology at the MST. Hence, we restrict consideration to symmetric or nearly symmetric A–B di-

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block molecules in which the fraction of type A monomers on each chain, f, is close to $^1/_2$. Furthermore, the analysis is restricted to the weak segregation limit regime, i.e., to the disordered phase and to temperatures very near the (bulk) MST in the ordered lamellar microphase. The diblock melt is placed in contact with a solid wall or a free (e.g., air) interface that contributes a surface free energy to the system.

Within the framework of a mean field theory, we compute the equilibrium composition profile of the copolymer in the direction normal to the surface. Even at temperatures where the bulk diblock is disordered, a surface that has a preferential affinity for one of the two components in the copolymer is found to give rise to an oscillatory composition profile that damps exponentially into the bulk. The oscillatory nature of the profile is a consequence of the connectivity of the A and B blocks and the constant density constraint in the melt. Depending on the ability of the surface to modify the enthalpic interactions between monomers in its vicinity, various types of surface phase transitions (analogous to those exhibited by low molecular weight fluid mixtures[22] or polymer blends[37]) are also possible. We discuss these surface phase transitions in the context of mean field theory and speculate on the qualitative changes that would ensue if fluctuations were properly taken into account. Wetting phenomena and the structure of three-dimensional ordered microphases (such as the BCC spherical microphase) near surfaces are also briefly discussed.

The organization of the paper is as follows. In section 2, we describe the diblock system under consideration and provide a Landau expression for the thermodynamic potential of the system with a surface. An Euler–Lagrange equation is derived for the composition profile that minimizes the potential. In section 3, we provide the solution of the equation (with appropriate surface boundary conditions) for temperatures above the MST temperature in the bulk. Section 4 contains the corresponding solution of the Euler–Lagrange equation for temperatures below the bulk MST. Surface phase transitions are also discussed. Finally, section 5 contains a general discussion of our results, speculates on the consequences of going beyond mean field theory and on extensions of the present formalism, and discusses experiments that might be used to test the various predictions.

2. Thermodynamic Potential and the Euler–Lagrange Equation

Our model system shown in Figure 1 is a diblock copolymer film of thickness L sandwiched between two planes at $x = \pm L/2$. The film is taken to be macroscopic in the surface directions normal to the x axis. The planes at $x = \pm L/2$ represent either solid surfaces or free boundaries. For convenience, we initially choose the origin of the x coordinate to be at the midplane of the film, but at later stages in our calculations it will prove advantageous to switch to a new coordinate system $X = x + L/2$ with origin on the left-hand plane in Figure 1. In the latter coordinates, we can study ordering near a single surface by taking the limit $L \rightarrow \infty$.

The copolymer under consideration consists of a melt of diblock chains, each of which has an A block of Nf statistical segments and a B block of $N(1-f)$ segments. The total number of statistical segments on each chain is N. To simplify the analysis, the segment lengths of the two components will be taken to be the same and the melt will be assumed incompressible. Modification of the theory to relax these assumptions is straightforward, yet tedious. A more important restriction on the present analysis is that only symmetric or nearly symmetric diblocks are considered; i.e., $f \approx {}^1/_2$. This restriction ensures that at temperatures below the bulk MST, the equilibrium morphology of a bulk sample is the lamellar microstructure. Finally, we restrict our analysis to the weak segregation limit, where a Landau expansion of the thermodynamic potential (free energy) is justified and no large composition gradients are present. Hence, the analysis does not apply for temperatures that are significantly lower than the bulk MST temperature.

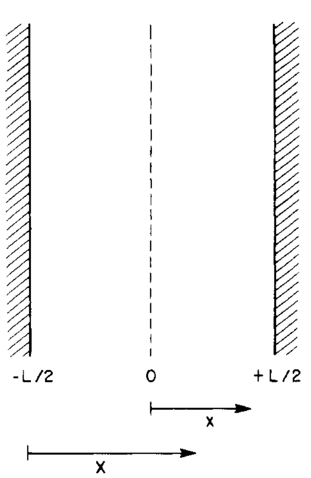

Figure 1. Block copolymer film considered in the present study. The origin of the x coordinate is taken to be the midplane of the film, denoted by the dashed line. In this coordinate system the film surfaces are at $\pm L/2$ and represent either solid walls or free (e.g., air) interfaces. For convenience in treating the ordering of block copolymers near a single surface, we sometimes employ the shifted coordinate $X = x + L/2$ with origin at the left-hand surface. In this latter frame of reference, one can take the limit $L \rightarrow \infty$ and consider a semiinfinite system.

To study the equilibrium properties of the diblock film shown in Figure 1, we construct an expansion of the thermodynamic potential in powers of an order parameter field $\psi(\mathbf{r})$. For a diblock copolymer, the appropriate order parameter is the local deviation of the average A-component density from its bulk value[10]

$$\psi(\mathbf{r}) = \langle \rho_A(\mathbf{r}) \rangle / \rho - f \tag{2.1}$$

where $\langle \rho_A(\mathbf{r}) \rangle$ is the average density of A segments at point $\mathbf{r}$ and ρ is the total segment density, $\rho = \langle \rho_A(\mathbf{r}) \rangle + \langle \rho_B(\mathbf{r}) \rangle$. The order parameter has the following property that will prove to be important in the subsequent analysis:

$$\int \mathrm{d}\mathbf{r}\, \psi(\mathbf{r}) = 0 \tag{2.2}$$

It is convenient to introduce the following Fourier representation of the order parameter ($q_x = 2\pi n_x/L$, $n_x = 0, \pm 1, \pm 2$, etc.)

$$\psi(\mathbf{r}) = L^{-1} \sum_{q_x} \int_{-\infty}^{\infty} \frac{\mathrm{d}q_y}{2\pi} \int_{-\infty}^{\infty} \frac{\mathrm{d}q_z}{2\pi}\, \tilde{\psi}(q) \exp(-i\mathbf{q}\cdot\mathbf{r}) \tag{2.3}$$

where $\mathbf{r} = (x,y,z)$ and

$$\tilde{\psi}(\mathbf{q}) = \int_{-L/2}^{L/2} \mathrm{d}x \int_{-\infty}^{\infty} \mathrm{d}y \int_{-\infty}^{\infty} \mathrm{d}z\, \psi(\mathbf{r}) \exp(i\mathbf{q}\cdot\mathbf{r}) \tag{2.4}$$

Note that eq 2.2 implies $\tilde{\psi}(0) = 0$. In all subsequent equations in this paper, lengths and reciprocal wavevectors are expressed in units of the statistical segment length, $b = \rho^{-1/3}$.

The thermodynamic potential describing the free energy of the system depicted in Figure 1 can be written as a sum of bulk and surface contributions (energy in units of k_BT)

$$F[\psi] = F_b[\psi] + F_s[\psi] \tag{2.5}$$

where the bulk potential is given in mean field theory by Leibler's expression[10]

$$F_{\mathrm{b}}[\psi] = \frac{1}{2!}\sum_{\boldsymbol{q}}\Gamma_2(\boldsymbol{q},-\boldsymbol{q})\tilde{\psi}(\boldsymbol{q})\tilde{\psi}(-\boldsymbol{q}) + \frac{1}{3!}\sum_{\boldsymbol{q}_1}\sum_{\boldsymbol{q}_2}\Gamma_3(\boldsymbol{q}_1,\boldsymbol{q}_2,-\boldsymbol{q}_1 - \boldsymbol{q}_2)\tilde{\psi}(\boldsymbol{q}_1)\tilde{\psi}(\boldsymbol{q}_2)\tilde{\psi}(-\boldsymbol{q}_1 - \boldsymbol{q}_2) + \frac{1}{4!}\sum_{\boldsymbol{q}_1}\sum_{\boldsymbol{q}_2}\sum_{\boldsymbol{q}_3}\Gamma_4(\boldsymbol{q}_1,\boldsymbol{q}_2,\boldsymbol{q}_3,-\boldsymbol{q}_1 - \boldsymbol{q}_2 - \boldsymbol{q}_3)\tilde{\psi}(\boldsymbol{q}_1)\tilde{\psi}(\boldsymbol{q}_2)\tilde{\psi}(\boldsymbol{q}_3)\tilde{\psi}(-\boldsymbol{q}_1 - \boldsymbol{q}_2 - \boldsymbol{q}_3) \quad (2.6)$$

In the above equation, the notation $\sum_{\mathbf{q}} \equiv (4\pi^2 L)^{-1}\sum_{q_x}\int \mathrm{d}q_y \int \mathrm{d}q_z$ is employed. Expressions for the vertex functions $\Gamma_n(\{\boldsymbol{q}_i\})$ are given by Leibler.[10] The (bare) surface contribution to the thermodynamic potential is assumed to be of the form[22]

$$F_{\mathrm{s}}[\psi] = \int \mathrm{d}\boldsymbol{r}\,[\delta(x + L/2) + \delta(x - L/2)]f_{\mathrm{s}}(\psi) \quad (2.7)$$

where the surface free energy density is

$$f_{\mathrm{s}}(\psi) = [-H_1\psi(\boldsymbol{r}) + a_1\psi^2(\boldsymbol{r})/2]/N \quad (2.8)$$

In eq 2.8, H_1 and a_1 are phenomenological parameters that describe the modification of the thermodynamic potential by the surfaces of the film. The "field" H_1 is related to the difference in chemical potential between A and B at the surface. The parameter a_1 will later be related to the usual "extrapolation length" encountered in surface critical phenomena.[22] It describes the ability of the surface to modify the local (Flory) interaction parameter χ between A and B segments in the polymer layer near the surface. For $a_1 > 0$, the local χ parameter is less than that in the bulk, whereas for $a_1 < 0$ the local χ is greater than the bulk value. In the latter case, one might expect that the surface layer could undergo an ordering transition at a temperature higher than the bulk MST.

In the usual situation, the surfaces of the film will have a preferential affinity for one of the two components in the diblock, i.e., $|H_1| > 0$. In the weak segregation limit under consideration, the interfacial tension between ordered microdomains in the bulk is very small. Hence, one expects that at temperatures less than (but near) the MST, the surfaces will be wet by the preferred component. Because we consider near-symmetric diblocks that form lamellar microphases, the above implies that the lamellae are expected to be oriented parallel to the surfaces (i.e., the periodic variation in composition is normal to the film surfaces). Indeed, this orientation of lamellae has been found in recent experiments on a polystyrene/polyisoprene diblock film at an air interface.[19]

On the basis of these arguments, it is reasonable to restrict our consideration to one-dimensional order parameter patterns that have variation only along the x axis.[25] Hence, we disregard variations of $\psi(\boldsymbol{r})$ in the y–z plane and replace the order parameter by its average $S^{-1}\int \mathrm{d}x \int \mathrm{d}y\, \psi(\boldsymbol{r})$, which will be denoted $\psi(x)$. Here S is the area of one of the film surfaces. With this simplification and multiplication by N to render all coefficients $\mathcal{O}(1)$, the potential can be written as

$$F[\psi]N/S = \frac{1}{2!}\sum_{q}\tilde{\Gamma}_2(q,-q)\tilde{\psi}(q)\tilde{\psi}(-q) + \frac{1}{3!}\sum_{q_1}\sum_{q_2}\tilde{\Gamma}_3(q_1,q_2,-q_1 - q_2)\tilde{\psi}(q_1)\tilde{\psi}(q_2)\tilde{\psi}(-q_1 - q_2) + \frac{1}{4!}\sum_{q_1}\sum_{q_2}\sum_{q_3}\tilde{\Gamma}_4(q_1,q_2,q_3,-q_1 - q_2 - q_3) \times \tilde{\psi}(q_1)\tilde{\psi}(q_2)\tilde{\psi}(q_3)\tilde{\psi}(-q_1 - q_2 - q_3) + \frac{1}{2}a_1[\psi^2(L/2) + \psi^2(-L/2)] - H_1[\psi(L/2) + \psi(-L/2)] \quad (2.9)$$

where $\tilde{\Gamma}_n(\{\boldsymbol{q}_i\}) \equiv N\Gamma_n(\{\boldsymbol{q}_i\})$.

Expressions for the vertex functions in eq 2.9 were derived by means of the random-phase approximation by Leibler.[10] To aid in the present analysis, we adopt the simpler approximation[11,14]

$$\tilde{\Gamma}_2(q,-q) \approx Aq^{-2} + Bq^2 - \bar{\chi} \quad (2.10)$$

$$\tilde{\Gamma}_3(q_1,q_2,-q_1 - q_2) \approx \mu \quad (2.11)$$

$$\tilde{\Gamma}_4(q_1,q_2,q_3,-q_1 - q_2 - q_3) \approx \Delta \quad (2.12)$$

where the composition (i.e., f) dependent coefficients A and B are defined by

$$A \equiv 3/[2R^2 f^2(1 - f)^2] \quad (2.13)$$

$$B \equiv R^2/[2f(1 - f)] \quad (2.14)$$

The radius of gyration of an unperturbed block copolymer chain is denoted R and in the present system of units is related to the number of statistical segments by $R^2 = N/6$. The coefficient $\bar{\chi}$ in eq 2.10 is both temperature and composition dependent and is defined by[23]

$$\bar{\chi} = 2\chi N - 2(\chi N)_{\mathrm{s}} + 3^{1/2}/[f(1 - f)]^{3/2} \quad (2.15)$$

Here χN is the product of the Flory (A–B) interaction parameter and the number of statistical segments and $(\chi N)_{\mathrm{s}}$ is the value of χN on the spinodal computed by Leibler[10] (e.g., $(\chi N)_{\mathrm{s}} = 10.495$ at $f = {}^1/_2$). The constant coefficients μ and Δ in eq 2.11 and 2.12 are also f dependent and are related to Leibler's coefficients $\{\Gamma_3, \Gamma_4(0,0)\}$ by $\mu = N\Gamma_3$ and $\Delta = N\Gamma_4(0,0)$. We have demonstrated elsewhere[17] that the approximations of eq 2.11 and 2.12 make very small numerical corrections in Leibler's bulk analysis. Ohta and Kawasaki[11] and Olvera de la Cruz and Sanchez[14] have verified the accuracy of eq 2.10 (see ref 23).

At this point it is worth commenting on the particular form of eq 2.10, the quadratic coefficient in the Landau expansion of the thermodynamic potential. In the usual Ginzburg–Landau free-energy functional that is used to describe binary mixtures near their critical consolute point, $\tilde{\Gamma}_2$ has the form $\tau + a^2q^2$. In this expression, τ is proportional to the (mean field) temperature difference from the critical point and a is a length that characterizes the range of the interactions between molecules. For the case of low molecular weight mixtures, a is of the order of the molecular size, while for homopolymer blends a is of the order of the radius of gyration. For the present case of a diblock copolymer melt, eq 2.10 has a term Bq^2, with $B^{1/2}$ from eq 2.14 also of the order of the radius of gyration. Hence, the range of interactions is much larger in homopolymer blends or block copolymer melts than in binary fluid mixtures, accounting for the success of mean field theory in the polymeric systems. Equation 2.10 for the block copolymer case, however, has an additional term Aq^{-2} that is peculiar to copolymer melts. This term is a manifestation of the connectivity of the two blocks in a copolymer molecule. It gives rise to a large (unfavorable) contribution to the free energy from inhomogeneous composition patterns that are of long wavelength (small q). Such patterns could only be created in a pure copolymer melt by stretching chains, which involves an entropy and hence free energy penalty.

With the above approximations, eq 2.9 can be written in the form

$$F[\psi]N/S = \int_{-L/2}^{L/2} \mathrm{d}x \left[\frac{1}{2}B\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right)^2 - \frac{1}{2}\bar{\chi}\psi^2 + \frac{\mu}{3!}\psi^3 + \frac{\Delta}{4!}\psi^4 + \frac{1}{2}A\int_{-L/2}^{L/2} \mathrm{d}x'\, G(x - x')\psi(x)\psi(x') \right] + \frac{1}{2}a_1[\psi^2(L/2) + \psi^2(-L/2)] - H_1[\psi(L/2) + \psi(-L/2)] \quad (2.16)$$

where $G(x - x')$ is the Green function for the one-dimensional Poisson equation

$$G(x - x') = L^{-1}\sum_q{}' q^{-2} \exp[iq(x - x')] \qquad (2.17)$$

and the prime on the sum indicates that the $q = 0$ term is excluded.

The equilibrium order parameter profile is obtained as the field $\psi(x)$ that minimizes $F[\psi]$ subject to the constraint of eq 2.2. Such a problem is standard in the calculus of variations.[24] The constraint is easily dealt with by introducing a Lagrange multiplier Θ and minimizing the functional $\Phi[\psi] = F[\psi]N/S - \Theta\int_{-L/2}^{L/2} \mathrm{d}x\, \psi(x)$ instead of $F[\psi]$. The extremum field satisfies the Euler–Lagrange equation

$$A\int \mathrm{d}x'\, G(x - x')\psi(x') - B\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \bar{\chi}\psi + \frac{\mu}{2!}\psi^2 + \frac{\Delta}{3!}\psi^3 - \Theta = 0 \qquad (2.18)$$

subject to the boundary conditions

$$a_1\psi - H_1 + B\frac{\mathrm{d}\psi}{\mathrm{d}x} = 0 \qquad x = L/2 \qquad (2.19)$$

$$a_1\psi - H_1 - B\frac{\mathrm{d}\psi}{\mathrm{d}x} = 0 \qquad x = -L/2 \qquad (2.20)$$

The Lagrange multiplier (Θ) is to be chosen such that the solution of eq 2.18–2.20 satisfies eq 2.2.

For a bulk system without boundaries, analysis of the equation of state 2.18 in the weak segregation limit yields the results of Leibler.[10] He found that the disordered phase of a diblock melt becomes unstable at the spinodal temperature, which in the present notation corresponds to a value of $\bar{\chi}$ satisfying $\bar{\chi} = \bar{\chi}_s$, with

$$\bar{\chi}_s = 3^{1/2}/[f(1 - f)]^{3/2} \qquad (2.21)$$

A bulk sample of a symmetric diblock in the present mean field theory undergoes a second-order phase transition to the lamellar morphology at $\bar{\chi}_s$. Hence, the MST coincides with the spinodal at $f = {}^1/_2$. In the subsequent analysis, we proceed as if the system were perfectly symmetric by assuming this coincidence to hold. However, for reasons discussed in ref 25, our analysis should still be applicable for nearly symmetric copolymers.

In the next section, we consider the solution of eq 2.18–2.20 in the regime where the bulk is disordered, $\bar{\chi} < \bar{\chi}_s$ (temperatures above the bulk MST). In section 4, we treat the case of temperatures below the bulk transition temperature. It will be assumed in both sections that $a_1 > 0$, which corresponds to the "ordinary transition" in the jargon of surface critical phenomena.[22] For this case, the layer of copolymer near the surface does not spontaneously order (in the absence of a surface field H_1) until the temperature is lowered to the bulk transition temperature. The cases $a_1 = 0$ and $a_1 < 0$ will be discussed briefly in section 5.

3. Analysis for the Disordered Bulk, $\bar{\chi} < \bar{\chi}_s$

At temperatures above the bulk MST, the free energy of a diblock melt without boundaries is minimized by the homogeneous order parameter field $\psi(x) = 0$. Hence, for $\bar{\chi} < \bar{\chi}_s$ and small surface fields H_1 (which will be assumed throughout), it is sufficient to consider the linearized version of eq 2.18

$$A\int \mathrm{d}x'\, G(x - x')\psi(x') - B\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - \bar{\chi}\psi - \Theta = 0 \qquad (3.1)$$

subject to the boundary conditions 2.19 and 2.20 and constraint 2.2. It proves convenient to change to the coordinate system $X = x + L/2$ as shown in Figure 1. The left-hand surface is then at the origin, and we can treat the case of a single surface by taking the limit $L \to \infty$. With these changes, the linear problem to be solved on $(0,\infty)$ is

$$A\int \mathrm{d}X'\, G(X - X')\psi(X') - B\frac{\mathrm{d}^2\psi}{\mathrm{d}X^2} - \bar{\chi}\psi - \Theta = 0 \qquad (3.2)$$

$$a_1\psi - H_1 - B\frac{\mathrm{d}\psi}{\mathrm{d}X} = 0 \qquad X = 0 \qquad (3.3)$$

$$\psi(X) \to 0 \qquad \psi'(X) \to 0 \qquad X \to \infty \qquad (3.4)$$

$$\int_0^\infty \mathrm{d}X\, \psi(X) = 0 \qquad (3.5)$$

Since eq 3.2 is a linear inhomogeneous equation, a general solution can be constructed from the superposition of a particular solution and the solution of the associated homogeneous equation. A particular solution of eq 3.2 is $\psi(X) = -\Theta/\bar{\chi}$, but because the associated homogeneous equation supports only growing or decaying plane wave solutions, the choice of $\Theta = 0$ is required to satisfy eq 3.4. The solution of the resulting homogeneous equation satisfying 3.3 and 3.5 is

$$\psi(X) = \frac{\psi_1}{\cos\phi}\exp(-X/\xi_+)\cos(\Omega X + \phi) \qquad (3.6)$$

where the bulk correlation length ξ_+ and the wavenumber Ω are defined by

$$\xi_+ = [4B/\bar{\chi}_s]^{1/2}[1 - \bar{\chi}/\bar{\chi}_s]^{-1/2} \qquad (3.7)$$

$$\Omega = [\bar{\chi}_s/4B]^{1/2}[1 + \bar{\chi}/\bar{\chi}_s]^{1/2} \qquad (3.8)$$

The phase ϕ in eq 3.6 is defined by

$$\tan\phi = \left[\frac{1 - \bar{\chi}/\bar{\chi}_s}{1 + \bar{\chi}/\bar{\chi}_s}\right]^{1/2} = 1/\xi_+\Omega \qquad (3.9)$$

At the surface, $X = 0$, eq 3.6 yields the following value of the order parameter

$$\psi_1 \equiv \psi(0) = H_1/[B(2\xi_+^{-1} + \lambda^{-1})] \qquad (3.10)$$

where $\lambda \equiv B/a_1$ is the so-called extrapolation length.[22] ($\lambda > 0$ because of the positivity assumption on a_1.) It is apparent that for temperatures above the bulk MST, $\bar{\chi} < \bar{\chi}_s$, a nonzero composition profile results only if $|H_1| > 0$, i.e., for a finite chemical potential difference at the surface.

Equation 3.6 is a very interesting result that could be used to interpret surface experiments on diblock copolymers at temperatures above the MST. It predicts an oscillatory composition profile near the surface whose amplitude is exponentially damped in the bulk. The period of oscillation, $2\pi/\Omega$, is seen from eq 3.8 to be temperature dependent. At the spinodal temperature, Ω is equal to the wavevector that characterizes the peak in the equilibrium (bulk) scattering function

$$q_0 \equiv \Omega(\bar{\chi} = \bar{\chi}_s) = [\bar{\chi}_s/2B]^{1/2} \qquad (3.11)$$

At temperatures above the MST, however, eq 3.8 yields a larger period of oscillation than $2\pi/q_0$. This prediction is an interesting feature of the surface problem in view of the fact that the peak position in the bulk scattering function is *temperature independent*.

The amplitude of the composition profile in eq 3.6 is damped on the scale of the bulk correlation length ξ_+,

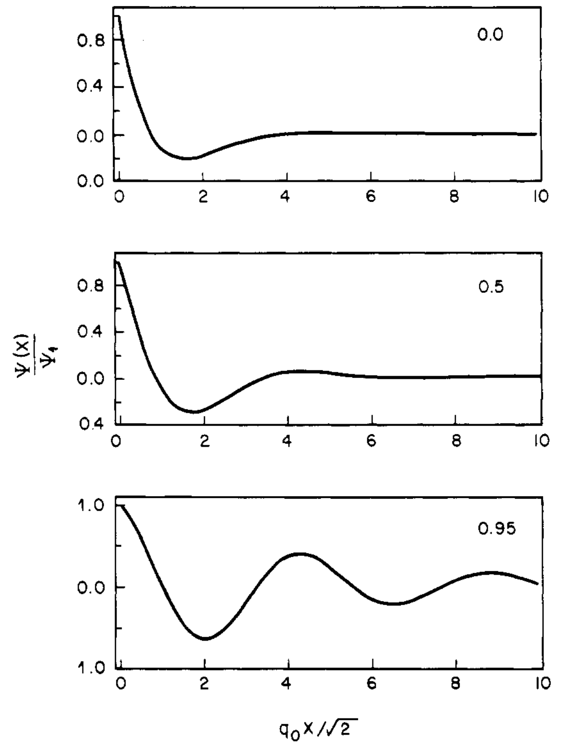

Figure 2. Normalized order parameter profiles for temperatures above the bulk MST. The figure shows $\psi(X)/\psi_1$ given by eq 3.6 plotted against $q_0X/2^{1/2}$. The number in the upper right-hand corner of each plot is the ratio $\bar{\chi}/\bar{\chi}_s$. This ratio approaches unity as the temperature is lowered toward the MST. The figure illustrates that the oscillations arising from the preference of the surface for the A component of the diblock penetrate many radii of gyration into the bulk as the MST is closely approached.

defined in eq 3.7. The correlation length increases as the temperature is lowered and diverges at the spinodal temperature in the present mean field approximation. Hence, as $\bar{\chi}_s$ is approached, the order induced at the surface by the chemical potential difference H_1 penetrates increasingly far into the bulk.

The phase of the oscillatory part of eq 3.6 is also of interest. From eq 3.9, ϕ is seen to decrease as the temperature is lowered, varying from $\pi/4$ at $\bar{\chi} = 0$ to zero at $\bar{\chi}_s$. As a result, in the limit $\bar{\chi} \to \bar{\chi}_s$, the thickness of the surface layer rich in component A (component B if $H_1 < 0$) approaches half the thickness of the adjacent layer rich in component B. This relationship was observed in the ordered polystyrene/polyisoprene system studied in ref 19.

In Figure 2 we show illustrative composition profiles obtained from eq 3.6. Plotted is the normalized profile $\psi(X)/\psi_1$ as a function of $q_0X/2^{1/2}$. With this scaling of the abscissa, the normalized profile depends solely on $\bar{\chi}/\bar{\chi}_s$. Increasing this ratio toward unity corresponds to lowering the temperature of a homogeneous diblock melt to approach the MST. Figure 2 demonstrates that the surface-induced order penetrates many radii of gyration into the bulk for $\bar{\chi}/\bar{\chi}_s$ sufficiently close to unity.

4. Analysis for the Ordered Bulk, $\bar{\chi} > \bar{\chi}_s$

At temperatures below the spinodal (MST), the nonlinear terms in eq 2.18 play an important role. Because the Landau expansion of the thermodynamic potential (eq 2.16) was truncated at finite order in ψ, the associated Euler–Lagrange equation 2.18 is only expected to be accurate for temperatures slightly below the spinodal, where the amplitudes of the equilibrium composition patterns are small. Within this temperature regime close to the transition, however, a rather detailed analysis of the nonlinear eq 2.18 is possible. In the following, we restrict our consideration to the above regime by requiring $0 < \epsilon^{1/2} \ll 1$ where

$$\epsilon = (\bar{\chi} - \bar{\chi}_s)/\bar{\chi}_s \tag{4.1}$$

Furthermore, it will be assumed throughout that $\lambda = B/a_1 > 0$.

The analysis proceeds by noting that at the spinodal temperature, a bulk diblock melt becomes unstable with respect to composition fluctuations of wavenumber q_0, defined in eq 3.11. As a result, for temperatures sufficiently close to the transition ($\epsilon \ll 1$), the dominant order parameter patterns will consist of superpositions of plane waves with wavevectors of magnitude q_0. To analyze this regime, we make use of a technique developed for the study of near-threshold convection in the Rayleigh–Bénard problem.[26-28] The method involves expressing the order parameter in terms of a slowly varying complex amplitude $Q(x)$

$$\psi(x) = \left[\frac{2\epsilon\bar{\chi}_s}{\Delta}\right]^{1/2}\{Q(x)\exp[i(q_0x + \phi)] + Q^*(x)\exp[-i(q_0x + \phi)]\} \tag{4.2}$$

where $Q^*(x)$ denotes the complex conjugate of $Q(x)$ and ϕ is an arbitrary phase. For $\epsilon^{1/2} \ll 1$, $Q(x)$ varies slowly on the distance scale q_0^{-1} and changes appreciably on the scale of the ordered phase correlation length ξ_-, defined by analogy with eq 3.7 as

$$\xi_- = \left[\frac{4B}{\epsilon\bar{\chi}_s}\right]^{1/2} \tag{4.3}$$

As a result, it is convenient to introduce the dimensionless coordinate $\zeta = x/\xi_-$ when studying the variation of the amplitude.

Substitution of eq 4.2 into (the rescaled) eq 2.18 leads to a differential equation for the complex amplitude $Q(\zeta)$. The term

$$A\xi_-\int \mathrm{d}\zeta'\, G(\zeta - \zeta')\psi(\zeta')$$

in eq 2.18 is treated by substituting eq 4.2 for $\psi(\zeta')$ and expanding $Q(\zeta')$ in a Taylor series about ζ. If we assume that derivatives of Q also vary slowly on the scale q_0^{-1}, then we can neglect terms like $\epsilon^{1/2}\,\mathrm{d}^3Q/\mathrm{d}\zeta^3$ relative to Q and derive the following (leading order in $\epsilon^{1/2}$) amplitude equation

$$\frac{\mathrm{d}^2Q}{\mathrm{d}\zeta^2} + Q[1 - |Q|^2] = 0 \tag{4.4}$$

Equation 4.4 turns out to be identical with the amplitude equation obtained from the one-dimensional Swift–Hohenberg model for Rayleigh–Bénard convection.[28,29] Solutions of the equation for a variety of boundary conditions have been considered in some detail by Kramer and Hohenberg.[28]

We first analyze eq 4.4 for a bulk diblock melt far from any boundaries. Following ref 28, the equation is found to possess spatially periodic solutions of the form

$$Q(\zeta) = (1 - p^2)^{1/2}\exp[ip(\zeta + \phi')] \tag{4.5}$$

where $|p| < 1$ is an arbitrary wavenumber and ϕ' some new phase. Equation 4.5 corresponds to the following order parameter pattern ($\phi'' = \phi + \phi'$)

$$\psi(\zeta) = \left[\frac{8\bar{\chi}_s\epsilon}{\Delta}\right]^{1/2}(1 - p^2)^{1/2}\cos\,[\zeta(\gamma + p) + \phi''] \tag{4.6}$$

where $\gamma \equiv q_0\xi_- = (2/\epsilon)^{1/2} \gg 1$ for the temperatures of interest. Hence, eq 4.4 leads to a family of order parameter profiles corresponding to the band of wavenumbers $\gamma + p$, $|p| < 1$. The pattern that will be selected in the physical system of interest is the member of this family that minimizes the bulk thermodynamic potential. By substitution of eq 4.6 into the bulk portion of eq 2.16 (i.e., that portion remaining when $a_1 = H_1 = 0$), we find that $F[\psi]$ is minimized by the order parameter profile with $p = 0$. Hence, $Q(\zeta) = 1$ is the solution of eq 4.4 that should be observed near criticality in the bulk and the corresponding order parameter pattern is

$$\psi(\zeta) = \left[\frac{8\bar{\chi}_s\epsilon}{\Delta}\right]^{1/2} \cos\,[\zeta\gamma + \phi''] \tag{4.7}$$

In the present mean field approximation, the amplitude of ψ vanishes continuously as $\epsilon \to 0$ (the signature of a second-order phase transition) and is $\mathcal{O}(\epsilon^{1/2})$, justifying the Landau expansion. Equation 4.7 agrees with the result of Leibler,[10] which was obtained by assuming the spatial dependence of eq 4.7 from the outset. The present analysis demonstrates that $2\pi/q_0$ is indeed the correct period (to order $\epsilon^{1/2}$ and in the mean field approximation) of the lamellar phase in the vicinity of the MST. If we insert the value[17] of Δ for a perfectly symmetric diblock ($\Delta(^1/_2) = 156.56$), the amplitude in eq 4.7 is found to be $0.841\epsilon^{1/2}$.

Returning to the surface problem, eq 4.4 must be solved subject to the appropriate boundary conditions on the film surfaces. It will again be convenient to shift the origin of the coordinate system to the left-hand surface in Figure 1 and consider the limit $L \to \infty$. If a shifted coordinate is defined as $Z = \zeta + L/2\xi_-$, the amplitude equation and associated boundary conditions (eq 2.19 and 2.20) can be written in the $L \to \infty$ limit as

$$Q''(Z) + Q[1 - Q^2] = 0 \tag{4.8}$$

$$Q'(Z) - Q[\gamma \tan\phi + \xi_-/\lambda] + \frac{H_1\xi_-}{B\cos\phi}\left[\frac{\Delta}{8\bar{\chi}_s\epsilon}\right]^{1/2} = 0 \qquad Z = 0 \tag{4.9}$$

$$Q(Z) \to 1 \qquad Q'(Z) \to 0 \qquad Z \to \infty \tag{4.10}$$

Here, the notation $Q'(Z) \equiv \mathrm{d}Q/\mathrm{d}Z$ is employed. In writing eq 4.8, we have taken advantage of the fact that the inhomogeneous solutions of eq 4.4 that satisfy $Q(Z) \to 1$ in the bulk are real.[28] The phase ϕ in eq 4.9 is determined from the condition 2.2, which implies

$$\int_0^\infty \mathrm{d}Z\, Q(Z) \cos\,(\gamma Z + \phi) = 0 \tag{4.11}$$

Equation 4.9 provides a relation between $Q'(0)$ and $Q_1 \equiv Q(0)$, the value of the amplitude at the surface. Another such relation can be obtained by multiplying eq 4.8 by $Q'(Z)$ and integrating on Z over $(0,\infty)$. This leads to

$$[Q'(0)]^2 = \frac{1}{2}(Q_1{}^2 - 1)^2 \tag{4.12}$$

Combination of eq 4.9 and 4.12 yields the following expression for the surface amplitude

$$Q_1 = \left[\frac{1}{2}(\gamma\tan\phi + \xi_-/\lambda)^2 + \frac{H_1\xi_-}{B\cos\phi}\left(\frac{\Delta}{4\bar{\chi}_s\epsilon}\right)^{1/2} + 1\right]^{1/2} - \frac{1}{2^{1/2}}(\gamma\tan\phi + \xi_-/\lambda) \tag{4.13}$$

in terms of the (as yet undetermined) phase ϕ. The profile $Q(Z)$ can be obtained by multiplying eq 4.8 by $Q'(Z)$ and integrating from 0 to Z. On substitution of eq 4.12 to eliminate $Q'(0)$, we find

$$[Q'(Z)]^2 = \frac{1}{2} - Q^2 + \frac{1}{2}Q^4 \tag{4.14}$$

This equation is easily integrated to yield the profile

$$Q(Z) = \frac{1 - \mu(\phi)\exp(-2^{1/2}Z)}{1 + \mu(\phi)\exp(-2^{1/2}Z)} \tag{4.15}$$

where $\mu(\phi) \equiv (1 - Q_1)/(1 + Q_1)$ with Q_1 given in eq 4.13. The order parameter profile follows from eq 4.2

$$\psi(Z) = \left[\frac{8\bar{\chi}_s\epsilon}{\Delta}\right]^{1/2} Q(Z)\cos\,(\gamma Z + \phi) \tag{4.16}$$

Finally, eq 4.11 and 4.15 can be combined to give the following equation for ϕ

$$\int_0^\infty \mathrm{d}Z \left[\frac{\exp(-2^{1/2}Z)}{1 + \mu(\phi)\exp(-2^{1/2}Z)}\right] \cos\,(\gamma Z + \phi) = 0 \tag{4.17}$$

We have been unable to perform this integral analytically but comment that it leads to $\tan\phi \sim \epsilon^{1/2}$ in the limit $\epsilon \to 0$. In actual calculations, eq 4.17 can be easily solved for ϕ by numerical methods.

Equation 4.13 makes some interesting predictions for the surface composition $\psi_1 = [8\bar{\chi}_s\epsilon/\Delta]^{1/2}Q_1\cos\phi$. In the case that $\lambda > 0$ and $H_1 = 0$, there is no chemical potential difference favoring either component at the surface. However, eq 4.13 predicts for this case that as $\epsilon \to 0$

$$\psi_1 = \left[\frac{2\bar{\chi}_s}{\Delta}\right]^{1/2} \frac{\epsilon\cos\phi}{\tan\phi + (\lambda q_0)^{-1}} \tag{4.18}$$

Hence, at the bulk spinodal temperature $\bar{\chi}_s$, the surface spontaneously orders as well as the bulk. Indeed, the bulk transition induces the surface transition. (The opposite scenario of surface order inducing bulk order cannot occur). In the absence of a surface field, ψ_1 is smaller than the amplitude of the bulk profile (eq 4.7), being of order ϵ compared with $\epsilon^{1/2}$ for the bulk amplitude. Equation 4.18 also shows that the surface transition is second order in that ψ_1 vanishes continuously as $\epsilon \to 0$.

In general, most surfaces will have a preferential affinity for one of the two components of the diblock. For $H_1 > 0$, A is the preferred component at the surface and eq 4.13 gives rise to a positive Q_1. At the spinodal temperature, $\epsilon = 0$, eq 4.13 predicts

$$\psi_1 = \frac{H_1\lambda}{B} + \mathcal{O}(H_1{}^2) \tag{4.19}$$

which agrees with eq 3.10 in this limit. For $\epsilon > 0$, the surface composition can be either smaller or larger than the bulk amplitude $[8\bar{\chi}_s\epsilon/\Delta]^{1/2}$, depending on the numerical values of the surface parameters H_1 and λ and the temperature difference ϵ.

Equation 4.16 is a prediction for the order parameter profile of a diblock melt near a surface at temperatures slightly below the MST. It suggests a spatially periodic variation of A-rich and B-rich regions with wavenumber $q_0 = \gamma/\xi_-$, corresponding to the position of the peak in the bulk (Leibler[10]) scattering function for the disordered phase. The amplitude of the composition profile is modulated by $Q(Z)$, defined in eq 4.15, which takes the value Q_1 at the surface and approaches unity in the bulk. The ordered phase correlation length ξ_- is the scale on which the bulk amplitude is approached. In the limit that $Q_1 \to$

0, which can be achieved, for example, in the situation discussed above, $H_1 = 0$, $\epsilon \rightarrow 0$, eq 4.15 reduces to the familiar form $Q(Z) = \tanh(Z/2^{1/2})$.

5. Discussion and Conclusions

In sections 3 and 4, surface ordering phenomena were predicted for diblock copolymer melts that are similar to phenomena predicted and experimentally observed for near-critical binary fluid mixtures[22] and homopolymer blends[37] near a surface. For example, all three systems show second-order surface and bulk phase transitions at the critical (spinodal) temperature in mean field theory. There are several qualitative differences between the block copolymer and the other two systems, however. Because of the connectivity of the blocks and the incompressibility constraint, the order parameter profiles obtained for the diblock system have an oscillatory component. In contrast, the concentration profiles for binary fluid mixtures or homopolymer blends near a surface decay or grow monotonically. Furthermore, diblock melts undergo microphase separation at the critical temperature to give rise to patterns with characteristic size $q_0^{-1} \sim R$, typically of order 100 Å, while fluid mixtures and blends undergo phase separation to produce domains of macroscopic extent.

From the similarity of the respective amplitude equations found in section 4, it is apparent that surface ordering phenomena in block copolymers may be closely related to the influence of boundary conditions on the stationary states of a fluid near the onset of Rayleigh–Bênard convection. Many of the powerful mathematical techniques that have been developed to treat the latter problem could likely find some applicability to block copolymers. In particular, the phase equation methods[30] that have been used successfully in studying the dynamics of cellular hydrodynamic patterns might facilitate similar investigations in diblock melts.

Of the experimental predictions in sections 3 and 4, those easiest to test are likely the results for the composition profile at temperatures above the bulk MST. The striking predictions of eq 3.6–3.10 for the temperature dependence of the period of oscillation, phase, and amplitude may be amenable to study by optical methods or Rutherford backscattering spectroscopy.[34] The optical methods include ellipsometry, evanescent wave-induced fluorescence,[35] and attenuated total reflectance spectroscopy. A disadvantage of the optical methods is that they don't directly probe the composition profile $\psi(X)$ but instead probe its Laplace transform or a few moments of the profile. Hence, the interpretation of the data is somewhat model dependent. However, the surface concentration can often be obtained from these techniques, allowing ψ_1 given by eq 3.10 to be determined and providing a relationship between the phenomenological parameters H_1 and λ. If χ can be determined by independent methods, such as by neutron scattering in the bulk,[7] then the composition profile in eq 3.6 is determined except for specification of one of the two surface parameters H_1 and λ. Hence, a one-parameter fit of the intensity from the optical methods will completely determine all coefficients in the theory.

In the present paper, we have treated the cases of temperatures above or below the MST. Although difficult to achieve experimentally, the case of $\bar{\chi} = \bar{\chi}_s$ can also be treated by analysis of an amplitude equation similar to eq 4.8 (but with different distance scaling). The result is analogous to that found in mean field theory for a critical binary fluid system.[22,31] For nonzero surface fields H_1, the amplitude is found to decay algebraically into the bulk, $Q(z) \sim x^{-1}$ for $x \rightarrow \infty$. This behavior is to be contrasted with the exponential decay found in sections 3 and 4 off-criticality. The period of oscillation of the composition profile is again found to be $2\pi/q_0$.

Another case not treated in the present paper is the possibility that the surface raises the critical temperature in the adjacent copolymer layer, leading to $a_1 \leq 0$ and hence $\lambda^{-1} \leq 0$. In the usual situation, where the surface modifies the local monomer interactions only within a thin surface layer of thickness $\mathcal{O}(b)$ (b is the statistical segment length) and the modifications are small, microscopic lattice models[22] can be developed to show that λ is positive and $\mathcal{O}(b)$. This situation gives rise to the "ordinary transition" at the surface studied in the present paper. However, if the surface is capable of strongly increasing the local χ parameter in its vicinity, the phenomenological parameter a_1 can vanish or become negative. The former case corresponds to the "special transition" in the surface critical phenomena literature, and the latter case gives rise to the "surface transition", where the surface layer orders at a temperature above the bulk critical temperature. These various surface-phase transitions are discussed in some detail in the review article by Binder.[22] Their analysis in the context of the present block copolymer problem is straightforward and proceeds by using the amplitude equation of section 4 in place of the Ginzburg–Landau equation employed for magnetic and binary fluid systems by Binder. We refer the interested reader to ref 22.

The results of the present paper were obtained by minimizing a thermodynamic potential in which composition fluctuations are neglected. This is the usual Landau or mean field approximation. We have recently demonstrated[17] that fluctuation corrections for a bulk diblock melt near the MST are negligible in the limit of infinite molecular weight but that the corrections to mean field theory can be substantial for the molecular weights typically used in experiments. We anticipate that there will be similar corrections for the present surface problem if composition fluctuations can be properly taken into account. Hence, the present theory may only prove to be quantitative for copolymers of very large molecular weight, but it provides a basis for developing more sophisticated theories and for the interpretation of experiments.

It is of interest to speculate on what the effect of properly including fluctuations in the present formalism would be. In ref 17, it was found that a bulk symmetric diblock melt undergoes a first-order phase transition at the MST in place of the second-order bulk transition predicted by mean field theory. The problem of surface ordering phenomena in semiinfinite systems with a bulk first-order phase transition was considered by Lipowsky.[32] He found that even though the bulk transition is first order, second-order "ordinary" transitions at the surface are possible if a_1 is sufficiently large. First-order "ordinary" surface transitions were also predicted if a_1 is less than a particular value. For the block copolymer problem, we anticipate similar results. However, in the case of very high molecular weight diblock melts, the bulk transition is only weakly first order, so the predictions of sections 3 and 4 for the order parameter profiles would likely be accurate except in a narrow temperature interval around the MST.

Many extensions of the present theory are possible. The case of asymmetric diblocks is an obvious example. Here the MST corresponds to a first-order transition, and the stable pattern in the bulk is spatially periodic in more than one dimension. The same formalism for the surface problem can be employed, but we must not average over inhomogeneities transverse to the x axis as in eq 2.9. Furthermore, in place of a single amplitude equation, analysis of higher dimensional periodic structures requires deriving separate equations for each amplitude in the superposition of plane waves describing the pattern. It was noted in ref 19 that asymmetric polystyrene/polyisoprene diblocks near an air interface show a complete lamellar wetting of the interface by the polyisoprene component. A complex region near the surface was observed where this one-dimensional pattern transforms to the stable three-dimensional pattern in the bulk. It would be of interest to investigate both theoretically and experimentally the composition profile away from such an interface and the crystallographic orientation of the hexagonal or spherical microphases near the surface.

Another interesting extension of the present work would be to study the strong segregation limit of temperatures well below the MST. In this regime, the interfacial free energy between microdomains is substantial and incomplete wetting of the surface is possible. Evidence for incomplete wetting in polystyrene/poly(ethylene oxide) diblock films at an air interface was given by Thomas and O'Malley.[20] It would be of great interest to study wetting phenomena in block copolymers and contrast it with the wetting behavior of binary fluid mixtures[33,38] or homopolymer blends.[37] The role that the block connectivity plays in determining contact angles and other wetting measurables is of particular interest.

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(23) We comment that eq 2.15 differs slightly from the expression given by Ohta and Kawasaki in ref 11. As discussed in ref 16, we enforce the additional condition that our approximation for $\tilde{\Gamma}_2$, evaluated at the wavevector corresponding to its minimum, must vanish at the spinodal temperature computed by Leibler.[10] This leads to an explicit expression for the undetermined function $s(f)$ introduced by Ohta and Kawasaki, $s(f) = 4f^2(1-f)^2(\chi N)_s - 2[3f(1-f)]^{1/2}$. Using Leibler's result of $(\chi N)_s = 10.495$ at $f = {}^1/_2$, we find $s({}^1/_2) = 0.893$, which is in excellent agreement with Ohta and Kawasaki's empirically determined value[11] of 0.9.

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(25) The argument for considering only one-dimensional inhomogeneities is complicated by the fact that if the present mean field theory is applied to a bulk system without boundaries, the lamellar microphase is only achieved at the MST for a perfectly symmetric copolymer; i.e., f is *exactly* equal to ${}^1/_2$. Leibler[10] found that a bulk sample of a perfectly symmetric diblock melt undergoes a second-order phase transition to the lamellar morphology at the spinodal temperature, which corresponds to a value of 10.495 for the product χN. He found, however, that the MST for a bulk sample of an asymmetric diblock occurs at a value of χN slightly less than its value on the spinodal and that the stable structure appearing at the MST is the body-centered-cubic (BCC) microphase. On the basis of these bulk predictions, it would seen that our restriction to one-dimensional patterns would be valid only for $f = {}^1/_2$. Furthermore, a perfectly symmetric block copolymer would be difficult to achieve experimentally. Our analysis, however, is saved by considering the effects of composition fluctuations. A recent study[17] has shown that fluctuations neglected in Leibler's theory modify the above mean field picture for bulk systems. One of the predictions is that a first-order transition is expected at the MST for a symmetric diblock, in place of the second-order transition discussed above. Furthermore, the value of χN at the transition is predicted to be larger than 10.495. The most important change for the present study, however, is that bulk samples of *near-symmetric* diblocks undergo direct first-order transitions to the *lamellar* microphase at the MST and not to be BCC structure. Although our present mean field theory for diblocks near surfaces does not include fluctuation corrections, the fact that such corrections open an experimental "window" to the lamellar microphase enhances the validity of considering only one-dimensional patterns.

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