Quasi-Static Mechanical Properties of Lamellar Block Copolymer Microstructure

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ABSTRACT: The quasi-static mechanical properties of lamellar block copolymer microstructure in weak segregation are calculated. In analogy with the smectic A liquid crystal phase, the mechanical properties are represented in terms of a layer compressibility and an elastic splay constant. Shifts in the order–disorder transition and metastability limit as well as the decrease in the degree of phase separation due to deformations are also calculated. Several applications of the calculated distortion free energy expression are discussed.

I. Introduction

The mechanical properties of the microstructure of block copolymers are important in understanding a variety of phenomena. In the processing of block copolymer materials, the microstructure of the material is deformed.[1-9] When a block copolymer is aligned by an external force, such as an electric field,[10,11] the mechanism of alignment is dictated by a balance between the external force and forces associated with distortion of the microstructural pattern. During annealing, the coarsening of the microstructural pattern is in large part dictated by the mechanical properties of the microstructural pattern. Defects, too, relate to the mechanical properties, in that the microscopic nature of a defect is such as to minimize the mechanical free energy associated with the structural distortions. Defects perhaps play an important role in some block copolymer rheological behavior.[8,9,12]

The goal of this paper is to calculate the free energy of deformed microstructure in block copolymer systems. In the present work we will restrict attention to small deformations of block copolymer lamellar microstructures in the weak segregation regime. A guiding theme for this calculation is the strong analogy between the composition pattern of lamellar block copolymer microstructure and the smectic A liquid crystal phase.[13] As in the case of smectic A's a lamellar pattern is of fundamental concern to us. Unlike smectic A's, we must pay attention not only to the distortion of the lamellae, but also to possible changes in the mean-square strength of the order parameter accompanying the distortion. (The order parameter in the present case is an oscillatory composition pattern making up the ordered phase.) The magnitude of the order parameter is generally not within our control. It relaxes to a value optimal for the given distortion in rapid time compared to the time required to relax the geometric distortion. Hence we calculate this optimal value of the order parameter to yield a minimum free energy for the given distortion.

The fundamental thermodynamic potential utilized for these calculations is that for block copolymers in weak segregation including the very important effects of fluctuations. The free energy, a functional of the concentration pattern, was determined by Fredrickson and Helfand,[14] utilizing the proposal by Brazovskii[32] on how to treat this class of systems. Actually, we will use a simplified (series) form of the free energy derived by Fredrickson and Binder.[17]

For small distortions of smectic A liquid crystals, de Gennes[15] has proposed a phenomenological energy form containing two "elastic constants". Our aim will be to cast the lamellar block copolymer free energy of distortion into this form. Specifically, we calculate the layer compressibility and splay elastic constant. In addition, we make quantitative predictions about the destabilizing effect of deformations, as well as the effect of deformations on the degree of phase separation. Special attention is given to the composition pattern near a disclination line defect. Finally, various modes of stress relaxation are considered.

Note added in proof: Just prior to publication we discovered that K. Kawasaki and T. Ohta (*Physica* **1986**, *139A*, 223) have carried out a calculation of the coefficients of an elastic Hamiltonian similar to those calculated in sections III.B and III.C. Their results differ from ours because they employ the mean-field free energy of Leibler,[16] rather than the free energy used here that includes fluctuation effects, which are important in weak segregation, especially with regard to molecular weight dependence.

II. Static Distortions of the Smectic A Phase

In this section, the phenomenological form of the distortion energy of a smectic A phase, proposed by de Gennes,[13,15] is reviewed. The system under consideration is a perfect single-domain smectic A sample with layer normals along the z axis (see Figure 1a). A distortion to the sample will displace the layer planes. The displacement is characterized by the field variable $u(\mathbf{r})$, which is the change in elevation of a layer plane at a particular x,y coordinate (see Figure 1b). We note that the unit normal vector to the layer, to first order in the distortion, has components

$$n_x = -\frac{\partial u}{\partial x} \qquad n_y = -\frac{\partial u}{\partial y} \qquad n_z = 1 \tag{2.1}$$

Discarding elements of the distortion field u that involve uniform translation or rotation and recognizing the symmetries of the smectic A phase, de Gennes writes for the free energy density due to distortions

$$f - f_0 = \frac{1}{2}\bar{B}\left(\frac{\partial u}{\partial z}\right)^2 + \frac{1}{2}K_1\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)^2 + \frac{1}{2}K'\left(\frac{\partial^2 u}{\partial z^2}\right)^2 + \frac{1}{2}K''\frac{\partial^2 u}{\partial z^2}\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right) \tag{2.2}$$

when u is slowly varying. The last two terms may be dropped. They involve distortions where u varies along z, and they will be dominated by the first term which is of lower order in the spatial variation of distortion. Also,

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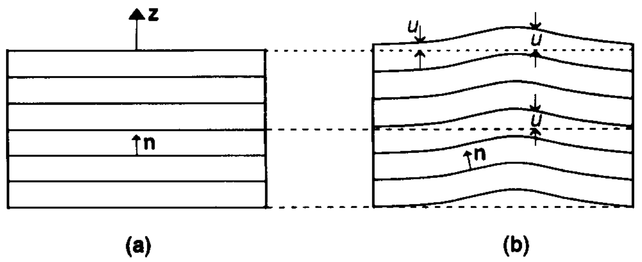

Figure 1. (a) Single-domain smectic A phase represented by layer planes. In (b), the material is deformed so that the elevation of the layer plane at a particular x–y coordinate is shifted by a distance $u(x,y,z)$ (indicated by the arrows). $\mathbf{n}$ is the unit vector normal to the layer planes.

using eq 2.1, the expression can be rewritten in the form

$$f - f_0 = \frac{1}{2}\bar{B}\left(\frac{\partial u}{\partial z}\right)^2 + \frac{1}{2}K_1(\nabla\cdot\mathbf{n})^2 \qquad (2.3)$$

The first term expresses the energy associated with compression or expansion of the layers, and $\bar{B}$ is the layer compressibility (not to be confused with bulk compressibility). The second term represents the energy associated with a splay distortion (the molecules undergo splay, the layer planes bend), and K_1 is the splay elastic coefficient. This term is analogous to the splay distortion energy term for nematic liquid crystals. There is no term analogous to bend and twist deformations here because such distortions cannot be accomplished without the creation of layer edge or screw dislocations.

A natural length scale comes out of the two distortion energy coefficients:

$$\lambda \equiv \sqrt{K_1/\bar{B}} \qquad (2.4)$$

which is usually comparable to the layer thickness.[13]

III. Theory

A block copolymer material with a lamellar microstructure has the same translational and rotational symmetries as the smectic A phase. Therefore, the development of de Gennes outlined in the previous section should be applicable. For block copolymers, the variable u represents distortions of planes of constant phase of the composition pattern, e.g. the planes on which the composition equals the bulk composition. From a molecular point of view, when a perfect, single-domain block copolymer sample is elongated or splayed, the free energy is increased due to distortion of polymer chain conformations and the change in intermixing of unlike monomers. In the following calculations, the energy of distortions comes out of a thermodynamic functional of the distorted composition pattern.

A. Thermodynamic Potential. In weak segregation, a Hamiltonian for the composition pattern was developed by Leibler, using mean-field theory. For a symmetric copolymer (the bulk volume fraction of each component is $^1/_2$), it is of the form[16]

$$\frac{H}{k_\mathrm{B}T} = \rho_\mathrm{c}\int \mathrm{d}\mathbf{r}\left\{\frac{1}{2}\psi(\mathbf{r})[\tau + eR_\mathrm{g}^{\,4}(\nabla^2 + q^{*2})^2]\psi(\mathbf{r}) + \frac{u}{4!}\psi(\mathbf{r})^4\right\} \qquad (3.1)$$

$\psi(\mathbf{r})$ is the local volume fraction of one component minus its bulk value. ρ_c is the number density of polymer chains, R_g is their radius of gyration, and q^* is the magnitude of the wave vector at the peak of the structure factor. τ and e are given by

$$\tau = 2[(\chi N)_\mathrm{s} - \chi N] \qquad (3.2)$$

$$e = 3c^2/2x^* \qquad (3.3)$$

χN is the Flory–Huggins interaction parameter times N, the degree of polymerization, and $(\chi N)_\mathrm{s} = 10.495$ is the value of χN at the spinodal, predicted by mean-field theory.[16] τ acts as a reduced temperature through the temperature dependence of χN. The following values for the constants are given in or can be calculated from refs 14 and 17: $c = 1.1019$, $x^* \equiv (R_\mathrm{g}q^*)^2 = 3.7852$, $u = 156.53$, and $e = 0.48116$. (In this work, u is used both as a thermodynamic coefficient and as the distortion field. The appropriate definition should be clear from the context.) Approximations that have been made are (i) the series is truncated at the fourth-order term, (ii) the random phase approximation is used to obtain the coefficients, (iii) the Fourier transform of the coefficient of the second-order term has been expanded about q^*, and (iv) the Fourier transform of the fourth-order term has been taken to be a constant, as suggested by Ohta and Kawasaki.[14,17,18]

Fredrickson and Helfand[14] calculated effects of composition fluctuations on the free energy within a Hartree approximation as proposed by Brazovskii. Using the Hamiltonian of eq 3.1, the thermodynamic potential for the composition pattern as given by Fredrickson and Helfand can be written as a power series in the time average of the composition pattern, $\bar{\psi}$:[17]

$$\frac{\Gamma(\bar{\psi})}{k_\mathrm{B}T} = \rho_\mathrm{c}\int \mathrm{d}\mathbf{r}\left\{\frac{1}{2}\bar{\psi}[\tau_\mathrm{R} + eR_\mathrm{g}^{\,4}(\nabla^2 + q^{*2})^2]\bar{\psi} + \frac{u_\mathrm{R}}{4!}\bar{\psi}^4 + \frac{w_\mathrm{R}}{6!}\bar{\psi}^6\right\} \qquad (3.4)$$

where the essence of the problem is contained in a series truncated after the sixth-order term. Here, the bar indicates a time average, so that only the "stationary" composition pattern associated with the ordered phase is considered; the dynamic concentration fluctuations are averaged out.[14,16] Γ is the free energy functional of $\bar{\psi}$. τ_R, u_R, and w_R are renormalized parameters, which are given by[17]

$$\tau_\mathrm{R} = \tau + \frac{du}{c\bar{N}^{1/2}\tau_\mathrm{R}^{\,1/2}} \qquad (3.5a)$$

$$u_\mathrm{R} = u\left[\frac{1 - \dfrac{du}{2c\bar{N}^{1/2}\tau_\mathrm{R}^{\,3/2}}}{1 + \dfrac{du}{2c\bar{N}^{1/2}\tau_\mathrm{R}^{\,3/2}}}\right] \qquad (3.5b)$$

$$w_\mathrm{R} = \frac{9du^3}{2c\bar{N}^{1/2}\tau_\mathrm{R}^{\,5/2}\left(1 + \dfrac{du}{2c\bar{N}^{1/2}\tau_\mathrm{R}^{\,3/2}}\right)^3} \qquad (3.5c)$$

$$d = 3x^*/2\pi = 1.8073 \qquad (3.5d)$$

$\bar{N}$ is a scaled degree of polymerization,[17] equal to $6^3(R_\mathrm{g}^{\,3}\rho_\mathrm{c})^2$. Fredrickson and Binder[17] expressed their terms in rescaled, reduced form. We prefer to retain the dimensional and unreduced variables. The relations between our definitions and of Fredrickson and Binder are given in the Appendix. τ passes through zero at the mean-field spinodal.[16] However, τ_R always remains positive. Over the range of interest in this work, u_R is negative. Within the framework of this construct, the energy associated with small deformations will emerge from quadratic term within the free energy expression. Contributions from a q dependence of the thermodynamic parameter u have been neglected.

In weak segregation, the average order parameter will be described as a simple sinusoid:

$$\bar{\psi} = 2A\cos(q^*z) \tag{3.6}$$

Note that the choice of wavenumber, q^*, minimizes the contribution from the term in the free energy containing the gradient. Inserting this expression into eq 3.4 yields a free energy density

$$f(A) = \rho_c k_B T\left(\tau_R A^2 + \frac{u_R}{4}A^4 + \frac{w_R}{36}A^6\right) \tag{3.7}$$

This polynomial is plotted in Figure 2 for several values of the reduced temperature, τ. As reported in ref 17, the polynomial has three minima when $u_R{}^2 - (4/3)\tau_R w_R > 0$. One is at $A = 0$ and two are at

$$A = \pm\left\{\frac{3}{w_R}\left[-u_R + \left(u_R{}^2 - \frac{4}{3}\tau_R w_R\right)^{1/2}\right]\right\}^{1/2} \tag{3.8}$$

There is only one minimum at $A = 0$ when $u_R{}^2 - (4/3)\tau_R w_R < 0$. The minimum at $A = 0$ corresponds to the disordered phase, and the two minima of eq 3.8 correspond to the ordered phase. The condition $u_R{}^2 - (4/3)\tau_R w_R = 0$ indicates the upper metastability limit of the ordered phase (see Figure 2). The order–disorder transition (ODT) is at the temperature for which the three minima are of equal free energy.

B. Calculation of Layer Compressibility, $\bar{B}$. In order to calculate the layer compressibility, we consider a small extension or compression of a uniform sample in the z direction normal to the lamellar planes. The boundaries at the side edges are displaced such that the sample density is not changed. Only the number of lamellae per unit length along z is changed. Using the nomenclature for distortions of the smectic A phase, the deformation field is

$$u(x,y,z) = \alpha z \tag{3.9}$$

where α is the extensional ($\alpha > 0$) or compressional ($\alpha < 0$) strain. The new composition pattern is described by

$$\bar{\psi}(\mathbf{x}) = 2A\cos[q^*(z+u)] = 2A\cos[(1+\alpha)q^*z] \tag{3.10}$$

We assume that the sample has not yet had sufficient time to relax into a lower-energy state by formation of defects or movement of dislocations (as described in the Discussion), but the degree of phase separation, indicated by A, had adjusted to an optimal value after the distortion. (The adjustment in A should occur on a time scale on the order of the longest polymer chain relaxation time.) Inserting the new composition pattern into the thermodynamic potential, eq 3.4, yields a free energy density polynomial in A:

$$f(A) = \rho_c k_B T\left[(\tau_R + \eta)A^2 + \frac{u_R}{4}A^4 + \frac{w_R}{36}A^6\right] \tag{3.11}$$

where

$$\eta = 6c^2 x^* \alpha^2 = 27.576\alpha^2 \tag{3.12}$$

comes from the term containing the gradient in the thermodynamic potential.[19] The effect of the distortion on the Landau free energy is illustrated in Figure 3. The new term raises the energy of the ordered state at finite A relative to the disordered state at $A = 0$.

The free energy of eq 3.11 has a local minimum at $A = 0$ and at

$$A_{\min} = \pm\left\{\frac{3}{w_R}\left[-u_R + \left(u_R{}^2 - \frac{4}{3}(\tau_R + \eta)w_R\right)^{1/2}\right]\right\}^{1/2} \tag{3.13}$$

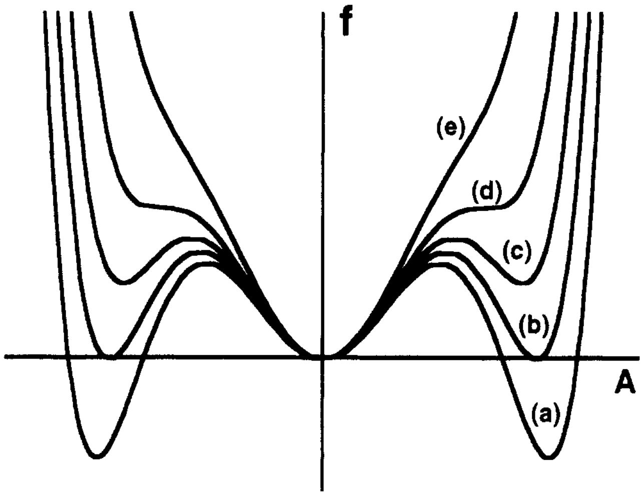

Figure 2. Landau diagrams for a symmetric block copolymer at several temperatures. The free energy density is plotted as a function of the amplitude A of the composition pattern, $\bar{\psi}$. The minimum at $A = 0$ corresponds to the disordered phase; the other two minima correspond to the ordered lamellar phase. In (a) the ordered phase is most stable. At the ODT the energies of the two phases are equal in (b). In (c) the ordered phase is metastable, and in (d) the upper metastability limit of the ordered phase is reached. In (e) only the ordered phase can persist.

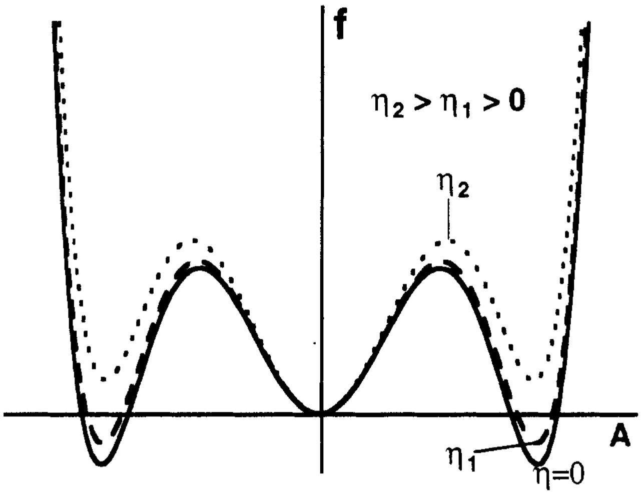

Figure 3. Effect of a distortion on the Landau free energy shown for a particular case. The energy due to a distortion adds a quadratic term to the Landau diagram which is greater for stronger distortions.

When $[u_R{}^2 - (4/3)(\tau_R + \eta)w_R]$ becomes negative, the minima of eq 3.13 vanish and the ordered phase loses even metastability. When $[u_R{}^2 - (4/3)(\tau_R + \eta)w_R] > 0$, eq 3.13 predicts real amplitudes, since u_R is negative.

The energy due to the distortion is equal to $f[A_{\min}(\eta);\eta] - f[A_{\min}(0);0]$. From eqs 3.11 and 3.13, we arrive at

$$\Delta f \equiv f[A_{\min}(\eta);\eta] - f[A_{\min}(0);0] = \rho_c k_B T A_0{}^2\eta + O(\eta^2) \tag{3.14}$$

where A_0 is the amplitude at the non-zero minimum of the free energy in the absence of a distortion (given by eq 3.8). The first term on the right represents the energy increase due to the distortion if the amplitude of the composition pattern remains unchanged. The shift in the free energy due to the relaxation to the preferred amplitude is second order in η and so is not explicitly shown. This is because in a Taylor expansion of f about $A = A_0$, the first-order term vanishes since $\partial f/\partial A|_{A_0} = 0$ by definition.

After one inserts the distortion field of eq 3.9 into the phenomenological free energy density expression for smectic A-like phases, eq 2.3 reads

$$f - f_0 = \frac{1}{2}\bar{B}\left(\frac{\partial u}{\partial z}\right)^2 = \frac{1}{2}\bar{B}\alpha^2 \qquad (3.15)$$

By inserting the expression for η, eq 3.12, into eq 3.14 and comparing to the above expression, one gets an expression for the layer compressibility:

$$\bar{B} = 12c^2x^*\rho_c k_B T A_0^{\ 2} = 55.151\rho_c k_B T A_0^{\ 2} \qquad (3.16)$$

The layer compressibility has units of energy per volume and is on the order of thermal energy, k_BT, per polymer chain volume.

C. Calculation of the Splay Constant, K_1. Consider a lateral oscillatory distortion of the phase of the lamellar composition pattern by

$$u(\mathbf{r}) = \beta\cos(kx) \qquad (3.17)$$

as shown in Figure 4. The amplitude of the distortion is β and the wave vector has magnitude k. Since u has no z dependence (cf. eq 2.2), this distortion is one of only splay. After this distortion, the composition pattern is given by

$$\bar{\psi}(\mathbf{r}) = 2A\cos[q^*(z + u)] = 2A\cos[q^*z + q^*\beta\cos(kx)] \qquad (3.18)$$

where, once again, we assume that the amplitude of the composition pattern has relaxed to achieve the lowest free energy compatible with the deformation, but the pattern has not had sufficient time to relax through movement of disclinations or creation of defects. For simplicity, we limit the case to small-amplitude distortions, so that $q^*\beta \ll 1$. Then

$$\bar{\psi}(\mathbf{r}) \approx 2A[\cos(q^*z) - q^*\beta\sin(q^*z)\cos(kx)] + O[(q^*\beta)^2] \qquad (3.19)$$

Inserting this expression into the thermodynamic potential, eq 3.4, yields

$$\langle f(A)\rangle = \rho_c k_B T\left[(\tau_R + \eta)A^2 + \frac{u_R}{4}A^4 + \frac{w_R}{36}A^6\right] \qquad (3.20)$$

for the spatially averaged free energy density, where

$$\eta = \frac{1}{2}eq^{*2}k^4R_g^{\ 4}\beta^2 \qquad (3.21)$$

comes from the term of the thermodynamic potential containing the gradient. (Since the distortion is spatially inhomogeneous, we chose to work with the space-average free energy density.)

The free energy density due to this distortion based upon the phenomenological equation of de Gennes, eq 2.2, is given by

$$f - f_0 = \frac{1}{2}K_1\left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2}\right)^2 = \frac{1}{2}K_1\beta^2k^4\cos^2(kx) \qquad (3.22)$$

which has a space-average value

$$\langle f - f_0\rangle = \frac{1}{4}K_1\beta^2k^4 \qquad (3.23)$$

Inserting the value for η from eq 3.21 into the expression for the free energy density, eq 3.14, and comparing the result to the above expression give an expression for the elastic splay constant:

$$K_1 = 3c^2\rho_c k_B T R_g^{\ 2}A_0^{\ 2} = 3.6426\rho_c k_B T R_g^{\ 2}A_0^{\ 2} \qquad (3.24)$$

For a typical block copolymer, this is on the order of 10^{-6} dyn, comparable to a typical splay constant for smectic A's.

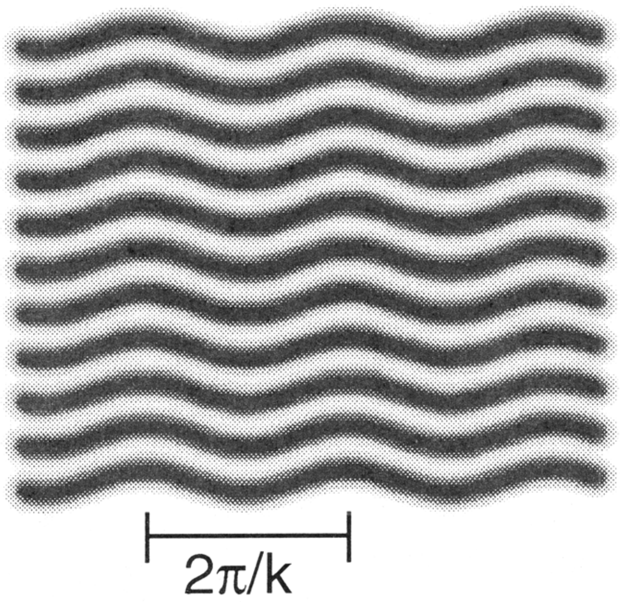

Figure 4. Lamellar microstructural pattern with an oscillatory distortion of the phase, as per eq 3.17. The distortion has wavelength k and amplitude β (which is exaggerated for clarity).

As with smectic A's, K_1 and B can be combined to form a natural length scale:

$$\lambda \equiv (K_1/\bar{B})^{1/2} = R_g/(2x^{*1/2}) = 0.257R_g \qquad (3.25)$$

which is on the order of one-quarter the molecular size, or about 8% of the domain repeat distance.[20]

D. General Deformation. Finally, for more general deformations, η is simply a sum of the effect of splay in two directions and layer compression. By recognizing the relation

$$\nabla\cdot\mathbf{n} = \frac{1}{R_1} + \frac{1}{R_2} \qquad (3.26)$$

where R_1 and R_2 are the local radii of curvature of the lamellae in any two orthogonal, tangential directions, one can express a general η as

$$\eta = \frac{3}{2}c^2R_g^{\ 2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2 + 6c^2x^*\alpha^2 = 1.8213R_g^{\ 2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)^2 + 27.576\alpha^2 \qquad (3.27)$$

Note that η times the square of the composition pattern amplitude, A, can be interpreted as a free energy increase due to distortions, in k_BT units per polymer chain.

E. Stability of a Distorted Ordered Phase. Distortions of the ordered phase increase the free energy density by an amount (cf. eq 3.14)

$$\Delta f = \rho_c k_B T A_0^{\ 2}\eta + O(\eta^2) \qquad (3.28)$$

This affects the stability of the ordered phase and shifts the point of coexistence with the disordered phase and the metastability limit of the ordered phase (e.g. see Figure 3).

The point of coexistence between the ordered and disordered phase is found at the conditions

$$f(A;\eta) = f(0;0) = 0 \qquad (3.29a)$$

$$\partial f(A;\eta)/\partial A = 0 \qquad (3.29b)$$

The first condition equates the free energy of the ordered and disordered phases, the second is for the local stability of the ordered phase. These two conditions lead to the equation

$$1 + \frac{\eta}{\tau_R} = \frac{(1+x)(1-x)^2}{16x} \tag{3.30}$$

where

$$x = du/2c\bar{N}^{1/2}\,\tau_R^{\,3/2} \tag{3.31}$$

For $\eta = 0$, eq 3.30 has one physically meaningful solution at $x = x_0 \equiv 4.6272$. This solution yields the condition for the ODT given by Fredrickson and Binder:[17]

$$\tau_R = 9.1643\bar{N}^{-1/3} \tag{3.32}$$

Expanding about $x = x_0$, for small η/τ_R,[21] eq 3.30 gives (to first order in η) the condition

$$\tau_R = 9.1643\bar{N}^{-1/3} - 0.28086\eta \tag{3.33}$$

From eqs 3.33, 3.5a, and 3.2, we get for small η

$$\chi_t N = \chi_s N + 37.823\bar{N}^{-1/3} + 0.79022\eta \tag{3.34}$$

where $\chi_t N$ is χN at the point of coexistence. This linear rule is reasonably good for $\eta \le 2\tau_R$.

The limit of metastability for the ordered phase is at the condition

$$\partial f(A,\eta)/\partial A = 0 = \partial^2 f(A,\eta)/\partial A^2 \tag{3.35}$$

These conditions give the equation

$$1 + \frac{\eta}{\tau_R} = \frac{(1+x)(1-x)^2}{12x} \tag{3.36}$$

In parallel with the above method, we find

$$\tau_R = 9.9236\bar{N}^{-1/3} - 0.27233\eta \tag{3.37}$$

at the upper metastability limit, or

$$\chi_0 N = \chi_s N + 35.789\bar{N}^{-1/3} + 0.69532\eta \tag{3.38}$$

where $\chi_0 N$ is χN at the upper metastability limit for the ordered phase. Once again, this linear rule is reasonably good for $\eta \le 2\tau_R$.

Equations 3.34 and 3.38 predict an upward shift in χN at both the coexistence and upper metastability points of the ordered phase due to any distortion of the composition pattern. The rise in the point of coexistence is slightly greater than for the metastability limit.

IV. Discussion

A. Mechanical Constants of Block Copolymer Lamellae. The splay constant, K_1, and the layer compressibility, $\bar{B}$, are shown in Figure 5 as functions of the reduced temperature, τ, for $\bar{N}$ of 10^3 and 10^5. Both mechanical constants decrease with rising reduced temperature, τ, due to the decreasing degree of phase separation (see eqs 3.16 and 3.24). At the transition point, τ_t, the curves should fall to zero. However, we can define a metastable branch, shown dashed. At the upper metastability limit of the ordered phase both constants fall discontinuously to zero as the ordered phase loses even metastability. For $\bar{N}$ equal to 10^3, this jump is quite noticeable, while it is much smaller for $\bar{N}$ equal to 10^5. This reflects a decrease in the first-order character of the phase transition with increasing molecular weight.

The length scale defined by the two mechanical constants, λ, is independent of temperature and is on the order of one-quarter of the molecular size. This is similar to what is found for the smectic A phase, where λ is also on the order of molecular size.[13]

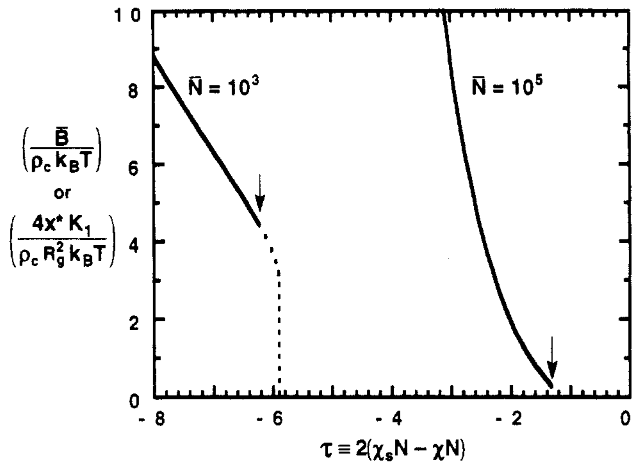

Figure 5. Dimensionless plots of the layer compressibility and splay constant as a function of reduced temperature for $\bar{N}$ equal to 10^3 and 10^5. (The value for x^* is given in section III.) The arrows indicate the ODT. Above the ODT the ordered phase can persist as a metastable state (indicated by the dashed line).

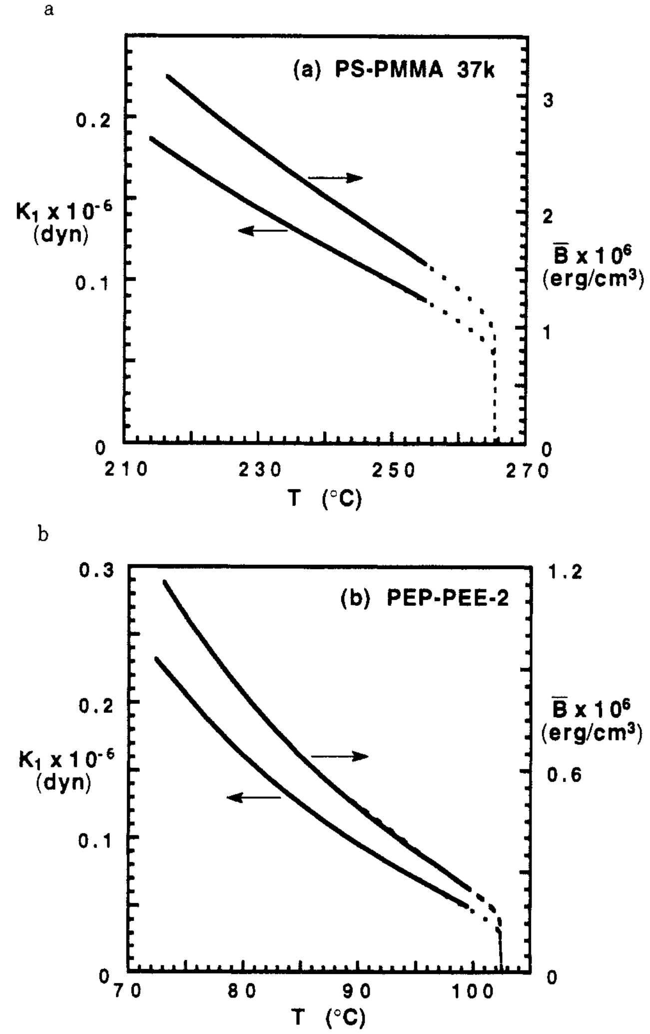

Figure 6. Layer compressibility and splay constant as functions of temperature for (a) PS–PMMA 37K and (b) PEP–PEE-2 symmetric diblock copolymers. The curves are dashed over the range where the ordered state is metastable.

In Figure 6, we show calculated mechanical constants for lamellae in two symmetric diblock copolymer systems: poly(ethylenepropylene)–poly(ethylenethylene) of molecular weight 50 000 ($\bar{N} = 1.1 \times 10^4$) (PEP–PEE-2),[22] and

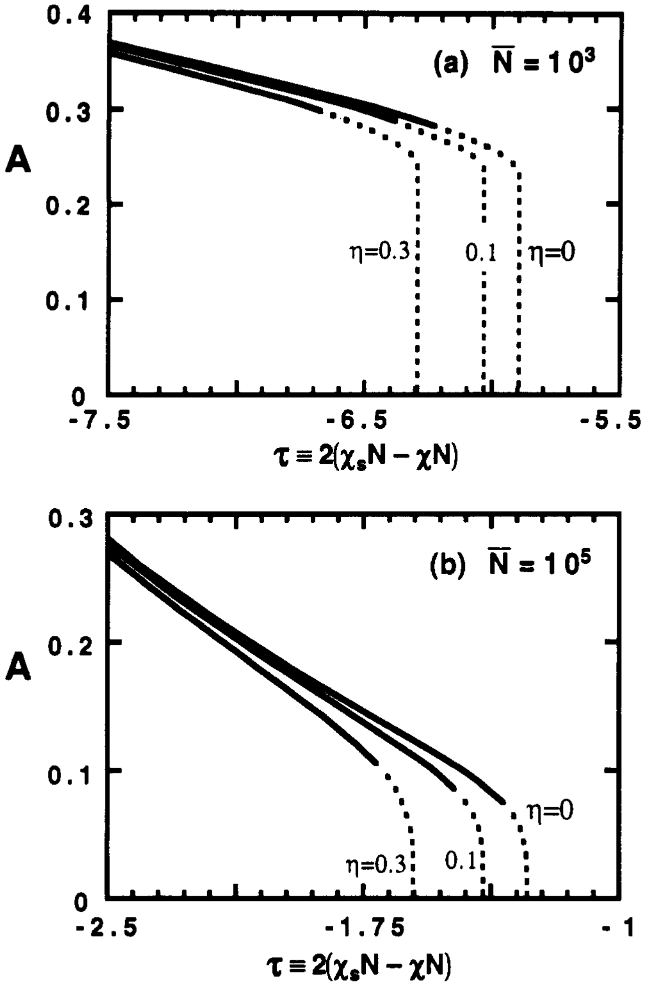

Figure 7. Equilibrium amplitude of the ordered phase as a function of reduced temperature for various distortion strengths (dictated by η of eq 3.27) for (a) $\bar{N} = 10^3$ and (b) $\bar{N} = 10^5$. The range over which the ordered phase is metastable is indicated by the dashed curve.

polystyrene–poly(methyl methacrylate) of molecular weight 37 000 ($\bar{N} = 1.0 \times 10^3$) (PS–PMMA 37K). The physical properties for the PEP-PEE-2 copolymer were obtained from the work of Rosedale and Bates[22] and for the latter polymer from refs 23–25. The decrease in both constants with increasing temperature reflects primarily the decreasing degree of phase separation. The sharp drop at the upper metastability limit for the ordered phase is more conspicuous for the PS–PMMA 37K copolymer because of its smaller $\bar{N}$.

B. Distortions and the Stability and Amplitude of the Ordered Phase Pattern. As shown by eq 3.13, the equilibrium amplitude of the composition pattern is reduced by deformations. The equilibrium amplitude of the ordered phase for various deformation strengths, indicated by η, and for $\bar{N}$ of 10^3 and 10^5 is shown as a function of the reduced temperature in Figure 7. The effect of deformations is rather small far from the upper metastability limit. However, as the upper metastability limit is approached, even small values of η can have a significant effect on the amplitude.

Distortions increase the free energy of the ordered phase, thus shifting the coexistence and metastability limits of the ordered phase to higher χN. Figure 7 shows the shift in the coexistence and upper metastability limit due to distortions. Calculated shifts in the ODT and metastability limit temperatures for the PS–PMMA 37K and PEP–PEE-2 copolymer systems and for various distortions are listed in Table I. The temperature shifts for relatively small distortions, especially compression or expansion, should be experimentally observable.

Table I
Calculated Shifts in the Coexistence and Upper Metastability Limit Temperatures of the Ordered Lamellar Phase of Two Symmetric Copolymers for Various Distortions

	extension and compression		splay	
	$\alpha^a = \pm 10^{-1}$	$\alpha = \pm 10^{-2}$	$R^a = 500$ Å	$R = 1000$ Å
PEP–PEE-2[b]	−6.8/−6.0	−0.07/−0.06	−1.4/−1.2	−0.35/−0.31
PS–PMMA 37K[c]	−11.0/−9.7	−0.11/−0.10	−0.01/−0.01	−0.003/−0.003

[a] α is the extensional or compressional distortion strength, and R is the local radius of curvature of the lamellae for splay. For each entry, the first number is the shift in the coexistence temperature, and the second is the shift in the upper metastability limit. [b] From ref 22. [c] From ref 25.

C. Shear Flow and Alignment. The ability to align block copolymer microstructure by shear and elongational flow has been known for over two decades.[1] Several mechanisms have been proposed for the alignment process,[6,7,9] including disordering of regions of the ordered state that are distorted by the shear flow, followed by reordering in a preferred alignment direction.[8,9] The elongational component of the shear flow field is thought to change the local periodicity of the lamellar phase and, beyond a sufficient strength, induce disordering, followed by reordering of lamellae in a different direction. When the rate of shear or elongation is much less than the lifetime of composition fluctuations, the results presented in section III (especially eqs 3.34 and 3.38, also e.g. Table I) could be used to predict the strength of local compression or expansion of the lamellar pattern required to induce local disordering. However, when the rate of shear or elongation exceeds the lifetime of fluctuations, then convection of composition fluctuations is expected to shift the transition temperature of the ordered phase, as predicted by Cates and Milner.[26] Koppi et al. also suggest the role of vorticity in shear flow alignment.[9] Dynamic phenomena such as these are not considered in this paper.

D. Composition Pattern near Disclination Lines. Disclination lines of half-integral strength have been observed in abundance in some block copolymer samples.[8,11,27] The pattern around disclination lines involves distortion of lamellae that increase in severity as the core is approached. A more rigorous determination of the composition pattern in the vicinity of a disclination can be made. However, on the basis of the above calculations, we can make some interesting semiquantitative predictions. One is a decrease in the amplitude of the composition pattern near a disclination line; the other is an increase of what may be called the disclination line core diameter close to the ODT.

Figure 8a shows a schematic of a lamellar pattern around a type $+^1/_2$ disclination line. On the basis of micrographs of type $^1/_2$ disclination lines, we approximate the pattern as semicircular in one half-space and undistorted in the other half-space. (This approximate pattern is exact in the limit of incompressible layers, i.e. $\lambda \rightarrow 0$.) η due to the splay in the semicircular portion of the lamellar pattern is

$$\eta = \frac{3}{2}c^2\left(\frac{R_g}{R}\right)^2 \qquad (4.1)$$

where R is the distance from the disclination line core. From eq 3.13, one can predict that the amplitude of the pattern, A, will decrease as the core is approached:

$$A(R) = A_0 \left[\frac{-u_R + \sqrt{u_R^{\,2} - \frac{4}{3}\left(\tau_R + \frac{3}{2}c^2\frac{R_g^{\,2}}{R}\right)w_R}}{-u_R + \sqrt{u_R^{\,2} - \frac{4}{3}\tau_R w_R}} \right]^{1/2} \qquad R/R_g \gg 1 \quad (4.2)$$

where A_0 is the amplitude far from the disclination core. Here, the effect of the gradient in the distortion field is neglected. This is a reasonable approximation when the distortion strength changes over a length scale much greater than the lamellar spacing.[28]

An interesting prediction, based upon the stability calculations of section III.E, is inhomogeneous disordering in the vicinity of disclination lines. In the approximation of a slowly-varying distortion field, a local disordering temperature can be defined according to eqs 3.34 and 4.1. Along with the increasing distortion strength, the local disordering temperature will shift more strongly to lower temperatures as the core is approached. Just below the bulk ODT, the region near the core will disorder before the bulk material. The result will be a growing core of disordered phase as the ODT is approached, as illustrated in Figure 8b. The radius of the "disordered core" can be estimated by equating it to the radius at which the distortion strength is sufficient to shift the order–disorder transition to the ambient condition. Once again, the assumption mentioned in the previous paragraph is made here. On the basis of eqs 3.34, 4.1, and 3.2, we predict the core radius of a type $^1/_2$ disclination line, $R_{\rm core}$, as a function of the reduced temperature to be

$$R_{\rm core} \sim \frac{1.70}{(\tau_t - \tau)^{1/2}} R_g \qquad (4.3)$$

where

$$\tau_t = 75.645\bar{N}^{-1/3} \qquad (4.4)$$

is the reduced temperature at the bulk ODT. The core radius is plotted as a function of the reduced temperature in Figure 9. As concrete examples, for the PS–PMMA 37K copolymer at 1 K below the ODT or PEP–PEE-2 at 0.5 K below the ODT, eq 4.3 gives a core radius of $\sim 9R_g$, or about three lamellar domain repeat distances.[20] Equation 4.3 should be taken as no more than an estimate, since it ignores effects that are important for small core radius, such as the surface energy at the edge of the disordered core, and the effect of gradients in the distortion field. It should be most valid very close to the ODT and for large core radii.

E. Stress Relaxation Modes. In this section, we discuss various stress relaxation mechanisms in a distorted microstructural pattern. The relaxation mechanisms for extension, compression, and splay can be very different.

Distortion energy due to layer extension and compression can be relaxed by movement of edge dislocations (see Figure 10c), as discussed for the case of smectic A systems by Clark and Meyer.[29] Here, movement of an edge dislocation introduces or eliminates layers and thus can change the number of layers per unit length toward its equilibrium value. An analogous mechanism for splay distortion does not appear possible.

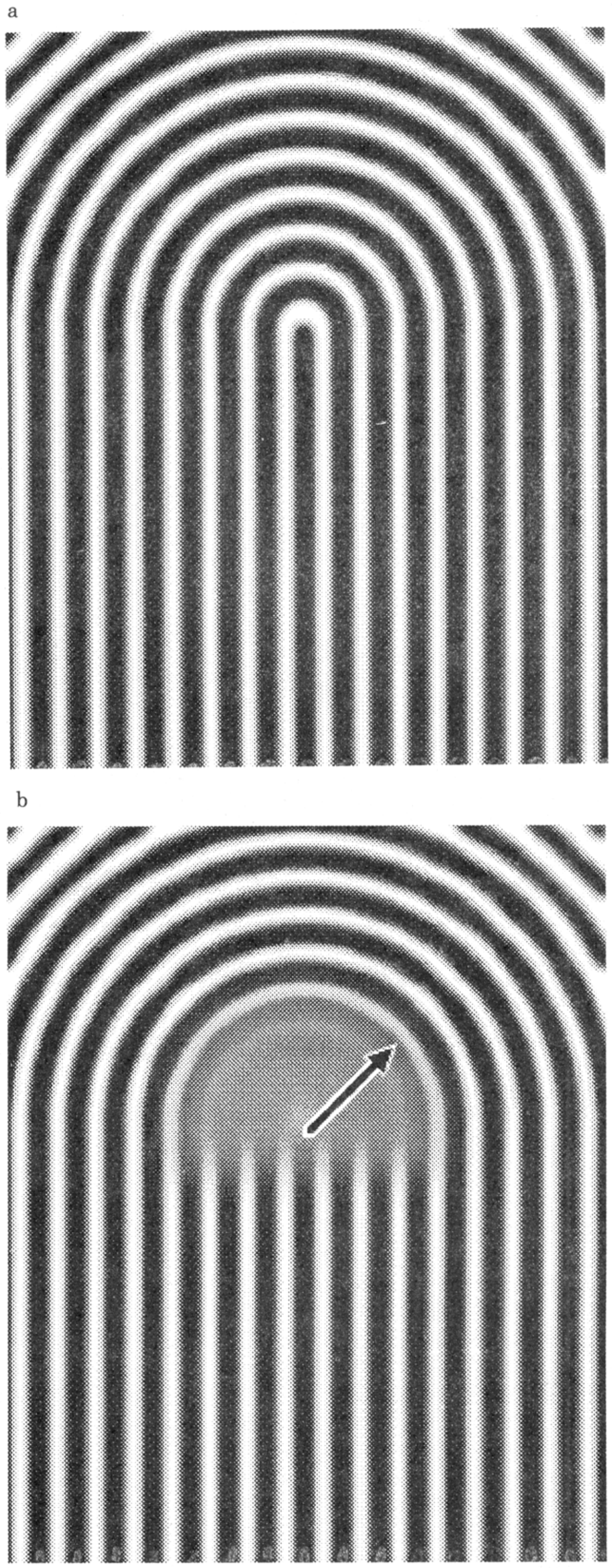

Figure 8. (a, Top) Lamellar pattern around a type $+^1/_2$ disclination line in the plane perpendicular to the line. In (b, bottom), the sample is close to the bulk ODT, and the highly distorted region near the core has disordered. The arrow indicates the radius, $R_{\rm core}$, of the "disordered core".

For an extensional distortion of sufficient strength, a mechanical instability that partially relaxes the distortion energy has been predicted and observed for smectic A systems.[13,29,30] Here, the layers prefer to form a ripple pattern in order to reduce their expanded period. This instability is illustrated for block copolymer microstructure in Figure 10d. It appears above a critical strain[13,29,30] (cf.

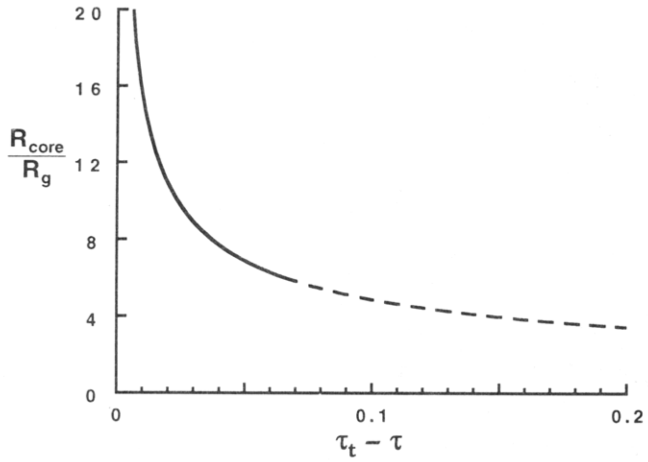

Figure 9. Radius of the "disordered core". R_{core}, shown as a function of the difference between τ, the reduced temperature, and, τ_t the reduced temperature at the bulk ODT.

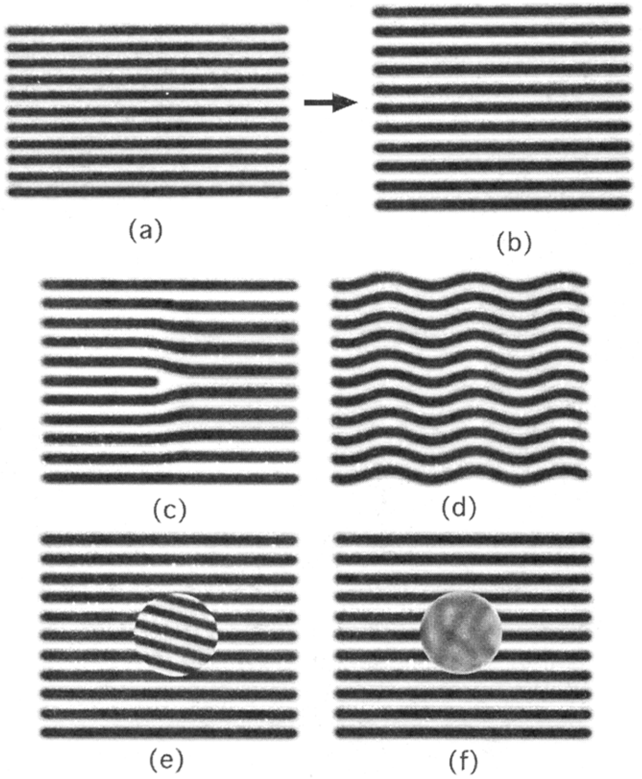

Figure 10. (a) Single-domain block copolymer sample with lamellar microstructure expanded in the direction normal to the lamellar layers (b). Various modes of relaxation are illustrated: movement of the edge dislocation in (c) to the right increases the number of layers in the sample. In (d), a mechanical instability leads to a ripple pattern of primarily splay distortion. (In actuality, the ripple amplitude decreases along z as each surface is approached. Only a center portion of the sample is shown here.) In (e) and (f), a nucleation center of a more stable phase (either ordered and undistorted or disordered) is shown. Nucleation centers beyond a critical size will grow.

eqs 2.4 and 3.9)

$$\alpha_c = 2\pi(\lambda/D) \tag{4.5}$$

where D is the sample thickness along the direction of extension. The period of the instability is (cf. eq 3.17)

$$2\pi/k = \sqrt{4\pi\lambda D} \tag{4.6}$$

An attempt is underway in our laboratory to induce and characterize this mechanical instability in a lamellar block copolymer. Comparison of a measured λ to the predicted value of eq 3.25 would provide a test of the work presented in this paper.

Another pathway to stress relaxation is nucleation and growth of an undistorted ordered phase, as illustrated in Figure 10e. The nucleation and growth process is dictated by two terms: the bulk free energy difference between the two phases and their interfacial energy per unit area (interfacial tension).[31] The bulk free energy density difference is simply the distortion free energy density:

$$\Delta f = \rho_c k_B T A_0^{\,2} \eta \tag{4.7}$$

The interfacial tension between the incommensurate phases has not been calculated to our knowledge. However, Fredrickson and Binder calculated the interfacial tension between an ordered and disordered phase of a symmetric block copolymer at the ODT:[17]

$$\sigma = 0.202(k_B T/R_g^{\,2}) \tag{4.8}$$

It is likely that the interfacial tension between two ordered but incommensurate phases near the ODT is of similar magnitude. Thus the free energy of the nucleus is estimated to be

$$\frac{F}{k_B T} = -\left(\frac{4}{3}\pi r^3\right)\rho_c A_0^{\,2}\eta + (4\pi r^2)\frac{0.202}{R_g^{\,2}} \tag{4.9}$$

where r is the nucleation center radius. For the specific case of distortion due to compression or extension, the maximum of this free energy, the activation free energy, is

$$F^*/k_B T = 0.223/\bar{N}^{1/3}\alpha^4 \tag{4.10}$$

near the ODT, where α is the extensional or compressional strain along the lamellar normal direction (cf. section III.B). If we hypothesize that processes with an activation free energy greater than $20k_B T$ are unobservable, then, if $\bar{N} \sim 10^4$, the process will occur at a reasonable rate for $|\alpha| > 0.15$. Two comments should be made. The first is that this result is quite sensitive to the magnitude of the surface free energy, which was crudely estimated. The second is that we think that we can hypothesize better mechanisms, based upon more rational alignment of the lamellae at joining surfaces of distorted and undistorted regions, or defect mechanisms as discussed earlier in this section. These issues are too detailed for consideration here.

If the distorted phase is metastable to the disordered phase, either through application of a sufficiently strong distortion or at sufficiently high temperature (see eq 3.38), then nucleation and growth of the disordered phase is a possible mechanism of relaxation. This is illustrated in Figure 10f. Here, the bulk free energy difference is given by

$$f(A_{\min};\eta) - f(0;0) \approx f(A_0;0) + \rho_c k_B T A_0^{\,2}\eta \tag{4.11}$$

and the surface energy (near the ODT) is given by the expression from Fredrickson and Binder, eq 4.8, above. Whether the resulting disordered phase persists or a new ordered phase grows is dictated by which of the two are of the lowest free energy at the temperature of the system.

Finally, if the distortion is of sufficient strength as to destabilize the ordered pattern (see eq 3.38), then the pattern would spontaneously dissipate, without the need for the slower nucleation and growth mechanism.

V. Summary

The static mechanical properties of the lamellar pattern in a weakly-segregated block copolymer have been calculated. Because of the similarity in symmetry of lamellar

Table II
Relations of Parameters in Reference 17 to Those of the Present Paper

variable or param	eq for related term(s) in Fredrickson and Binder[a]	
τ	$\tau_0^{FB} = \rho_c \tau$	$\tau^{FB} = (1/c^2)\tau$
e	$e_0^{FB} = \rho_c R_g^4 e$	$e^{FB} = (1/36c^2)e$
u	$u_0^{FB} = \rho_c u$	$u^{FB} = (1/c^4 \bar{N}^{1/2})u$
w_R		$w_R^{FB} = (1/c^6 \bar{N})w_R$
A		$A^{FB} = c\bar{N}^{1/4}A$
q^*	q^{*FB}	$q_0^{FB} = 6^{1/2} R_g q^*$
$\mathbf{r}$	$\mathbf{x}^{FB} = \mathbf{r}$	$\mathbf{r}^{FB} = (1/6^{1/2} R_g)\mathbf{r}$
f		$f_H^{FB} = (6^{3/2} R_g^3 / k_B T)f$

[a] The relations shown in these columns for τ and u also hold for τ_R and u_R.

microstructure and the smectic A liquid crystal phase, those properties are dictated by two constants: $\bar{B}$, the layer compressibility, and K_1, the elastic splay constant. These elastic constants were derived using a thermodynamic potential developed by Fredrickson and Helfand. A general deformation involves compression of layers and bending of lamellar layer planes (splay distortion). The effect of all deformations on the free energy of the ordered phase is dictated by η, the free energy of distortion in $k_B T$ units per polymer chain, given in eq 3.27.

Distortions result in a decrease in the degree of phase separation, which is in general a small effect except near the upper metastability limit. Also, the ODT and upper metastability limit of the ordered phase are shifted to lower temperatures by distortions. Several relaxation mechanisms of distortion energy of the lamellar phase were discussed.

Appendix

Numerous references are made to the work of Fredrickson and Binder.[17] However, because of the rescaling of variables in that work, many of the parameters and variables have different meanings. Table II gives some equations relating terms of Fredrickson and Binder (indicated with an "FB" superscript) to those used in this work. The terms without superscripts are used in this work. These equations can be used to convert equations in ref 17 to a form consistent with this work.

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