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On the Landau−Brazovskii Theory for Block Copolymer Melts

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The phase behavior of block copolymer melts has been attracting considerable attention recently due to the observation of new phases formed by low molecular weight diblock copolymers near the order−disorder transition (ODT), in particular bicontinuous cubic and perforated lamellar structures.[1−5] Obtaining an understanding of the origins of these "complex" phases remains a challenging theoretical problem. In this Communication we address some issues concerning the phase diagram of block copolymer melts, using the Landau−Brazovskii (LB) theory where allowance is made for composition fluctuations, following the method of Brazovskii.[6] This theory was first developed for block copolymers by Fredrickson and Helfand,[7] following mean field calculations by Leibler of the phase diagram for weakly segregated diblocks.[8] The resulting phase diagram for diblock copolymers with equal segment lengths is then only a function of the composition, specified by the volume fraction f of one component and χN, where χ is the Flory−Huggins interaction parameter and N is the degree of polymerization. Fredrickson and Helfand showed that the phase diagram for diblock copolymers is modified from that calculated by Leibler such that it becomes a function of the degree of polymerization, expressed in normalized units $\bar{N} = N(a^6/v_0^2)$, where a is a statistical segment length and v_0 is a molecular volume.[7] In particular, it was shown that χN for symmetric diblocks at the order−disorder transition scales with $\bar{N}^{-1/3}$.[7] This theory also predicts direct transitions to the lamellar (lam) and hexagonal-packed cylinder (hex) phases, whereas mean field theory predicts that a BCC phase (of $Im\bar{3}m$ symmetry) is the first stable phase below the order−disorder transition (ODT), except for $f = 0.5$ where a second-order transition to a lamellar structure is predicted. The Fredrickson−Helfand theory has been shown to explain a number of experimental observations that indicate the importance of composition fluctuations near the ODT (reviewed in refs 9 and 10).

Recently, Matsen and Schick showed, using numerical self-consistent mean field theory calculations, that a bicontinuous "gyroid" phase, of $Ia\bar{3}d$ symmetry, can be stable with respect to lam and hex phases.[11] The $Ia\bar{3}d$ structure was found to be stable between the "classical" phases, starting at a triple point just below the order−disorder transition. This approach does not allow for composition fluctuations, and a direct transition from the disordered isotropic phase to the $Ia\bar{3}d$ phase observed experimentally[2,5] is not predicted. Experimental work by Bates and co-workers has shown that the stability of the $Ia\bar{3}d$ phase in block copolymers is a function of $\bar{N}$.[1] As $\bar{N}$ is decreased, an $Ia\bar{3}d$ phase first becomes stable near the order-disorder transition and then the stability region extends to a wider composition and temperature range.

In this Communication, we investigate the stability of the $Ia\bar{3}d$ phase using the Landau−Brazovskii approximation, for block copolymer melts near the ODT. Our general method (which can be applied to thermotropic and lyotropic liquid crystals) has been detailed elsewhere.[12]

In the vicinity of a weak phase transition between the disordered, isotropic phase and an ordered phase, the density function of a block copolymer can be written as

$$\rho(\boldsymbol{r}) = \rho_0 + \delta\rho(\boldsymbol{r}) \qquad (1)$$

where ρ_0 is the uniform component insensitive to the phase transition, and $\delta\rho(r)$ is the short wavelength component related to the local monomer density.[8] The LB free energy functional describing this phase transition can be written in units of k_BT as[13]

$$H_{LB}[\delta\rho] = \int\delta\rho\left[\frac{\tau}{2}\delta\rho^2 + \frac{\xi_0^{\,2}}{8q_0^{\,2}}[(\nabla^2 + q_0^{\,2})\delta\rho]^2 - \frac{\gamma}{3}\delta\rho^3 + \frac{\lambda}{4!}\delta\rho^4\right] \qquad (2)$$

Here τ is the reduced temperature, q_0 is the critical wavenumber, ξ_0 is the bare correlation length, and γ and λ are higher order vertex functions. In the units of Fredrickson and Helfand for diblock copolymer melts these quantities are given by[7]

$$\tau = \frac{2[(\chi N)_s - \chi N]}{c^2} \qquad (3a)$$

$$\gamma = \frac{N\Gamma_3}{c^3} \qquad (3b)$$

$$\lambda = \frac{N\Gamma_4(0,0)}{c^4} \qquad (3c)$$

$$\xi_0^{\,2}q_0^{\,2} = 6x^* \qquad (3d)$$

Here c is an O(1) constant defined by Fredrickson and Helfand,[7] the subscript s denotes spinodal and Γ_3, $\Gamma_4(0,0)$ are vertex functions introduced by Leibler.[8] The correlation function, ξ_0, which defines a molecular length is equal to $\sqrt{6}R_g$, which is the end-to-end distance of a Gaussian polymer coil. For the system to be close to the short-wavelength instability, it is assumed that $|\tau| \ll \xi_0^2q_0^2$.[6]

In the LB theory the ordering transition occurs upon condensation of several Fourier components (harmonics) of the density function close to the sphere $|q| = q_0$ in reciprocal space. The condensate wavevectors are considered as the reciprocal lattice vectors for the ordered structure. The short-wavelength component of the density function in the absence of fluctuations can then be written in terms of a series of orthonormal basis functions:

$$\delta\rho(\boldsymbol{r}) = \sum_n \rho_n\varphi_n(\boldsymbol{r}) \qquad (4)$$

Here n is an index labeling harmonics, ρ_n are the amplitudes playing the role of order parameters, and the $\varphi_n(\boldsymbol{r})$ are orthonormal basis functions. The basis functions can be calculated using expressions for the geometrical structure factor tabulated in ref 14, further

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details being given elsewhere.[12,15] The basis functions can naturally be ordered using the parameter

$$\epsilon_n = \left(\frac{q_n^{\,2}}{q_0^{\,2}} - 1\right)^2 \tag{5}$$

which characterizes the relative distance of the wavevector (of magnitude q_n) of the nth harmonic from the sphere $|q| = q_0$. The sum in (4) is restricted in LB theory to the set of harmonics with $\epsilon_n \ll 1$.[12]

Within classical LB theory, lam, hex (two-dimensional $P6m$), and $Im\bar{3}m$ structures compete for stability. For these structures $\epsilon_2^{\mathrm{lam}} = 9$, $\epsilon_2^{\mathrm{hex}} = 4$, and $\epsilon_2^{Im\bar{3}m} = 1$. Thus in the LB theory, analysis of the stability of the lam, hex, and $Im\bar{3}m$ structures is performed in the one harmonic approximation. The mean field free energies for lam, hex, and $Im\bar{3}m$ phases can be calculated using expressions for the corresponding basis functions and are given by the equations[13,16]

$$F_{\mathrm{MF}}^{\mathrm{lam}} = \frac{\tau}{2}\rho_1^{\,2} + \frac{\lambda}{4!}\frac{3}{2}\rho_1^{\,4} \tag{6a}$$

$$F_{\mathrm{MF}}^{\mathrm{hex}} = \frac{\tau}{2}\rho_1^{\,2} - \frac{\gamma}{3!}\sqrt{\frac{2}{3}}\rho_1^{\,3} + \frac{\lambda}{4!}\frac{5}{2}\rho_1^{\,4} \tag{6b}$$

$$F_{\mathrm{MF}}^{Im3m} = \frac{\tau}{2}\rho_1^{\,2} - \frac{\gamma}{3!}\sqrt{\frac{4}{3}}\rho_1^{\,3} + \frac{\lambda}{4!}\frac{15}{4}\rho_1^{\,4} \tag{6c}$$

The phase diagram for competing lam, hex, and $Im\bar{3}m$ structures in the mean field approximation is well-known.[16] Except for $\gamma = 0$, the $Im\bar{3}m$ phase appears first upon crystallization due to the relatively large cubic coefficient. At lower temperatures, the hex phase is stable, as the structure with intermediate values of the cubic and quartic coefficients. At the lowest temperatures the lam phase is most stable because it has the smallest quartic coefficient.

A traditional analysis within Landau theory does not take into account the fact that the wavevectors of the second harmonic [220] for the $Ia\bar{3}d$ structure are uniquely close to the sphere $|q| = q_0$, occupied by the wavevectors of the main harmonic [211]. Indeed, for the $Ia\bar{3}d$ structure $\epsilon_2^{Ia\bar{3}d} = {}^1\!/_9$, and this is at least 1 order of magnitude smaller than for other competing structures (it should also be noted that $\epsilon_3^{Ia\bar{3}d} = {}^{16}\!/_9$). Thus unlike the lam, hex, and $Im\bar{3}m$ phases, the stability of the $Ia\bar{3}d$ phase should be analyzed in the two harmonic approximation. Using the basis functions for the first two harmonics of the $Ia\bar{3}d$ structure,[12,15] the mean-field free energy of the $Ia\bar{3}d$ phase can then be shown to be[12]

$$\begin{aligned} F_{\mathrm{MF}}^{Ia3d} = {} & \frac{\tau}{2}\rho_1^{\,2} - \frac{\gamma}{3!}\frac{1}{\sqrt{6}}\rho_1^{\,3} + \frac{\lambda}{4!}\frac{17}{8}\rho_1^{\,4} + \\ & \frac{1}{2}\left(\tau + \frac{1}{4}\epsilon_2^{Ia\bar{3}d}\xi_0^{\,2}q_0^{\,2}\right)\rho_2^{\,2} - \frac{\gamma}{3!}\frac{2}{\sqrt{3}}\rho_2^{\,3} + \\ & \frac{\lambda}{4!}\frac{15}{4}\rho_2^{\,4} + \frac{\gamma}{3!}\frac{\sqrt{3}}{2}\rho_1^{\,2}\rho_2 + \frac{\lambda}{4!}3\rho_1^{\,2}\rho_2^{\,2} \end{aligned} \tag{7}$$

A comparative analysis of the free energy of the different phases shows that allowance for the second harmonic [220] of the $Ia\bar{3}d$ phase in addition to the principal one [211], results in stabilization of this structure in a narrow window of the phase diagram between the stability regions of the lam and hex phases, starting at a triple point just below the ordering transition.[11,12] The triple point is located at $|\tau| \sim \epsilon_2^{Ia\bar{3}d}\xi_0^{\,2}q_0^{\,2}$, where the second harmonic [220] of the $Ia\bar{3}d$ phase becomes important for the first time.

An expression for the free energy of the system in the presence of thermal fluctuations was obtained by Podneks and Hamley,[12] using the Hartree approximation:

$$F_{\mathrm{Hartree}} = F_{\mathrm{MF}} + 2\alpha\sqrt{r} - \frac{\lambda}{2}\frac{\alpha^2}{r} \tag{8}$$

Here F_{Hartree} is the free energy computed within the Hartree approximation[6] and F_{MF} is the mean field free energy. The coefficient[6] $a = q_0^{\,2}v_0/4\pi\xi_0$ and expressions for the gap r are given elsewhere.[6,7,12] In contrast to the well-known equation of Brazovskii (eq 13b in ref 6), which gives the *difference* between the Hartree free energies of the disordered liquid and crystalline phases, eq 8 gives the *absolute* value of the free energy in the LB theory.

The principal requirement for validity of the LB theory when allowance for critical fluctuations is made can be expressed in block copolymer units as the inequality[12]

$$\kappa \equiv \frac{(a\lambda)^{2/3}}{\xi_0^{\,2}q_0^{\,2}} = \frac{(d\lambda)^{2/3}}{6x^*}\bar{N}^{-1/3} \ll 1 \tag{9}$$

where $d = 3x^*/2\pi$. We assume here that the value of r at the Brazovskii transition (r_{Br}) is of the order of $|\tau_{\mathrm{Br}}|$, so the inequality (9) guarantees satisfaction of the Brazovskii criterion $r_{\mathrm{Br}} \gg \alpha\lambda(\xi_0 q_0)^{-1}$.[6] This ensures the smallness of higher order corrections to the Hartree free energy up to the phase transition line. It turns out that this condition results in an estimate of the lowest value of $\bar{N}$ for which Landau–Brazovskii theory applies, which is in agreement with that obtained by Fredrickson and Helfand, $\bar{N} \gtrsim 10^4$.[7]

As an illustration of the application of the theory, we present phase diagrams calculated using eq 8 for representative low and high molecular weight diblock copolymers in Figure 1. Figure 1a presents results for a diblock copolymer with $\bar{N} = 5 \times 10^3$. It can be seen that the $Ia\bar{3}d$ phase is stable over a wide region between the lam and hex phases, as observed experimentally.[2,5] This phase diagram is in qualitative agreement with the phase diagram for low molecular weight PS–PI diblocks presented by Khandpur et al., in which a direct transition between the disordered and $Ia\bar{3}d$ phases is observed.[5] A detailed comparison is hindered because transitions from experiments on a series of block copolymers with different values of $\bar{N}$ are combined on a single plot, which is thus not strictly speaking a single-phase diagram.

The phase diagram calculated for $\bar{N} = 10^6$ is shown in Figure 1b. Again, the $Ia\bar{3}d$ phase is stable between the hex and lam phases; however the $Ia\bar{3}d$ phase stability region terminates at a triple point below the ODT and there is no direct transition between disordered and $Ia\bar{3}d$ phases. We estimate that a direct transition first occurs for a critical value of $\bar{N}$, $\bar{N}^* \approx 1 \times 10^4$ near $f = 0.43$. Because κ is a function of f for block copolymers, there is a complex mapping between $\bar{N}^*$, f, and the critical value of $\kappa > \kappa^* = 0.06$, for a direct transition from the isotropic to the $Ia\bar{3}d$ phase.[12] We note in summary that a direct transition between the isotropic phase and the $Ia\bar{3}d$ phase observed experimentally can be accounted for when composition fluc-

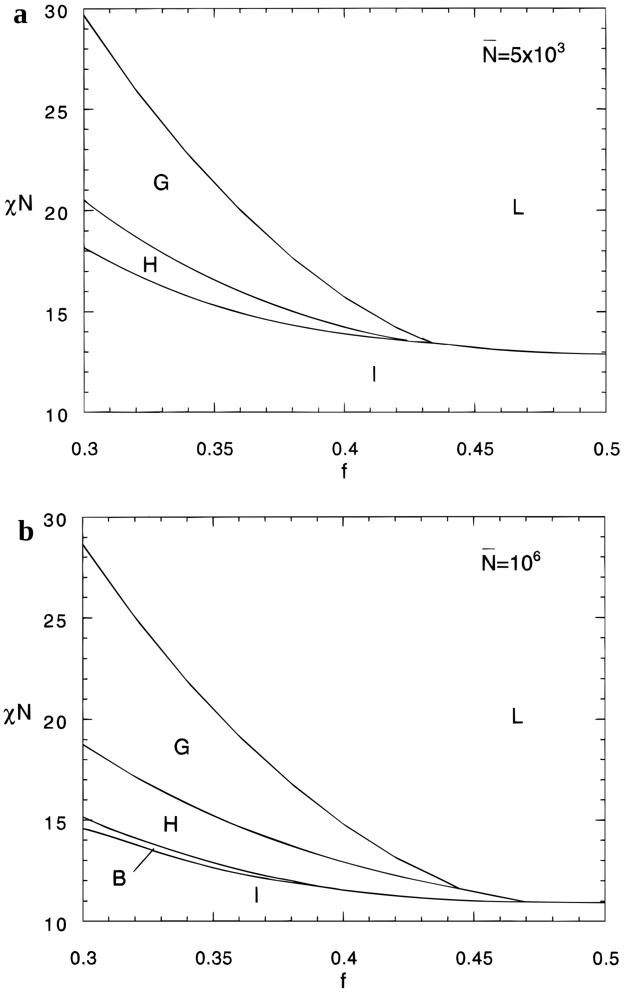

Figure 1. Phase diagrams calculated using the Landau–Brazovskii approximation for diblock copolymers with (a) $\bar{N} = 5 \times 10^3$ and (b) $\bar{N} = 5 \times 10^6$. Key: L, lamellar phase; H, hexagonal phase; G, *Ia*$\bar{3}$*d* (gyroid) phase; I, isotropic (disordered) phase.

tuations are considered, below a critical degree of polymerization $\bar{N}^* \approx 1 \times 10^4$.

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