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Landau theory of the orthorhombic *Fddd* phase

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Numerical self-consistent-field theory calculations by Tyler and Morse [Phys. Rev. Lett. **94**, 208302 (2005)] predict a stable orthorhombic network phase with space group *Fddd* in very weakly segregated diblock copolymer melts. Here, we examine the predicted stability of this phase within a simple Landau theory of weakly ordered crystals, and within a straightforward extension of Leibler's theory of weakly segregated diblock copolymer melts. An *Fddd* structure with a ratio of unit cell parameters $(a:b:c)=(1:2:2\sqrt{3})$ is found to compete very closely with the hexagonal (H) and lamellar (L) phases along the predicted H-L phase boundary, and to be stable within a very narrow range of parameters around this metastable boundary.

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I. INTRODUCTION

The power of the Landau approach to phase transitions lies in its ability to make qualitative predictions about entire classes of materials, independent of differences in chemical details. A Landau theory of crystallization was first constructed by Alexander and McTague (AM) [1]. The mathematical structure of their theory suggested some purely geometrical rules for selecting plausible candidate crystal structures for systems that undergo very weakly first-order crystallization transitions. In particular, the theory predicted that the first phase to form upon cooling of a liquid of any system with a sufficiently weak first-order crystallization transition should be a body-centered-cubic (BCC) crystal.

One particularly fruitful application of the Landau theory to a crystallization phenomena was the study by Leibler of the phase diagram of weakly segregated diblock copolymer melts [2]. Leibler constructed a Landau theory for weakly ordered diblock copolymer melts, which is similar in structure to the AM theory, and also calculated the coefficients in the Landau expansion from an underlying self-consistent-field theory of polymer liquids. Leibler considered candidate BCC crystal and hexagonal (H) columnar phases, which were also considered by AM, and a lamellar (L) phase, which was not explicitly considered by AM. Leibler predicted that the cooling of a disordered (D) liquid phase of a melt of slightly asymmetric diblock copolymers should generally lead to a phase sequence $D\rightarrow\mathrm{BCC}\rightarrow H\rightarrow L$, consistent with AM's conclusion that a BCC phase should form first.

Subsequent numerical self-consistent-field theory (SCFT) calculations by Matsen and Schick [3] established a predicted phase diagram for diblock copolymers that is consistent with the behavior obtained by Leibler in the weak segregation regime, and that also includes a gyroid cubic network phase. The predicted region of stability of the gyroid phase lies between those of the hexagonal and lamellar phases in moderately segregated systems, but does extend into the weak segregation region in which Leibler's theory is rigorously valid. The gyroid phase has also been shown to be stable above a critical value of χN in an extension of Leibler's single-wave-number theory that includes Fourier components of the order parameter field arising from two families of reciprocal lattice wave vectors with slightly different wave numbers [4,5].

Bates and co-workers [6,7] have mapped the phase behavior of poly(isoprene-*b*-styrene-*b*-ethylene oxide) (ISO) and poly(cyclohexylethylene-*b*-ethylethylene-b-ethylene) ($\mathrm{CE_EE}$) triblocks copolymers. In both of these systems, they have found a significant region in the composition phase triangle where an orthorhombic network phase having an *Fddd* space group symmetry is stable. Tyler and Morse [8] calculated the phase diagram of the ISO triblocks using the numerical SCFT method and obtained results in qualitative agreement with the experimental results.

Tyler and Morse also reanalyzed the phase diagram of diblock copolymers, while allowing for an *Fddd* orthorhombic network as one of the candidate phases. They found the *Fddd* network to be a stable phase of very weakly segregated diblocks in a narrow window that lies between the Hex and lamellar phases. The *Fddd* phase window also borders the gyroid phase, which lies between the Hex and lamellar phases in more strongly segregated systems. The fact that the *Fddd* phase was found to be stable in numerical SCFT only for very weakly segregated diblock melts suggests that the reasons for its stability might be understood within the framework of a Landau theory.

II. LANDAU THEORY OF CRYSTALLIZATION

In the Landau theory, we define an order parameter field $\psi(r)\equiv\langle\delta\rho(r)\rangle$ that is associated with the deviation of the ensemble average of a particle concentration $\rho(r)$ from its spatial average value. This order parameter field may be associated with either the concentration of atoms in atomic liquid, or with a deviation in the local concentration of either of the two types of monomers in a diblock copolymer melt. In either case, the order parameter $\psi(r)$ in a periodically structure may be expanded in plane waves as a sum

$$\psi(\mathbf{r})=\sum_{\mathbf{G}}\psi_{\mathbf{G}}\exp(i\mathbf{G}\cdot\mathbf{r}) \tag{1}$$

in which $\mathbf{G}$ denotes a wave vector that belongs to the reciprocal lattice of the crystal, and the sum is over all nonzero reciprocal lattice wave vectors. The difference between the free energy density of a very weakly ordered crystal and that of a homogeneous liquid, denoted $f \equiv F/V$, can be Taylor expanded as a sum

$$f[\psi] = \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{\mathbf{G}_1,\ldots,\mathbf{G}_n} \Gamma^{(n)}(\mathbf{G}_1,\ldots,\mathbf{G}_n)\psi_{\mathbf{G}_1},\ldots,\psi_{\mathbf{G}_n} \qquad (2)$$

where V is the volume of the system. As a result of the translational invariance of this free energy functional, a coefficient $\Gamma^{(n)}(\mathbf{G}_1,\ldots,\mathbf{G}_n)$ may be nonzero only for arguments that satisfy the constraint $\mathbf{G}_1 + \mathbf{G}_2 + \cdots + \mathbf{G}_n = 0$.

The most general form of the Landau theory considered here is obtained by keeping all terms of order $n \leqslant 4$ in (2). The second-order coefficient $\Gamma^{(2)}(\mathbf{q};T)$ in (2) is positive for all q at all temperatures T greater than a spinodal temperature T_s. To describe a transition to a periodic ordered phase, $\Gamma^{(2)}(\mathbf{q};T)$ is assumed to have a minimum value at a wave number $|\mathbf{q}| = q^*$, and to reach a minimum $\Gamma^{(2)}(q^*;T_s) = 0$ at the spinodal. At temperatures near T_s and wave numbers near q^*, $\Gamma^{(2)}$ may thus be approximated by an expression

$$\Gamma^{(2)}(\mathbf{q}) \simeq \tau + \alpha(|\mathbf{q}| - q^*)^2 \qquad (3)$$

with a minimum value $\tau \propto T - T_s$.

In systems that exhibit sufficiently weak first-order transitions, crystallization yields structures in which the dominant Fourier components of $\psi(\mathbf{r})$ correspond to a set of reciprocal lattice vectors of magnitude $|\mathbf{G}| = q^*$. Following both Alexander and McTague and Leibler, we consider a one-wave-number approximation in which Fourier expansion (1) is approximated by a sum over only a set of "primary" wave vectors with a common wave number $|\mathbf{G}| = q^*$, which corresponds to the set of nonzero reciprocal lattice vectors with the smallest magnitudes for the crystal structure of interest.

The wave-number dependence of the $\Gamma^{(2)}(q)$ selects a preferred length scale, but not a crystal structure. In the Landau theory, the competition between different possible crystal structures is instead controlled by the cubic and quartic terms. As a result of translational invariance, the cubic term is nonzero only for lattices for which there exist triplets of three reciprocal wave vectors $\mathbf{G}_1$, $\mathbf{G}_2$, $\mathbf{G}_3$ of equal magnitude $|\mathbf{G}_1| = |\mathbf{G}_2| = |\mathbf{G}_3| = q^*$, such that

$$\mathbf{G}_1 + \mathbf{G}_2 + \mathbf{G}_3 = \mathbf{0}. \qquad (4)$$

This condition can be satisfied only by triplets of coplanar reciprocal lattice vectors that form an equilateral triangle. Unless $\Gamma^{(3)}$ is very small, the favored crystal structures near the spinodal are those for which this condition is satisfied. These structures are stabilized by the existence of a negative cubic term.

Alexander and McTague noted that Eq. (4) is satisfied by the primary reflections of a two-dimensional (2D) hexagonal lattice and those of a BCC lattice, but were unable to identify any other periodic structure for which the condition is satisfied. It is not, in particular, satisfied by the primary reflections of a primitive FCC crystal or a diamond lattice, for which the primary wave vectors are {111}, or those of the $Ia\bar{3}d$ gyroid structure, for which the primary wave vectors are {211}. As a result, neither the double diamond nor gyroid networks are competitive candidate phases in a single-wave-number approximation, or in the limit of very weak segregation. For very small $\Gamma^{(3)}$ values, which is the case for diblocks with near-symmetric compositions, the consideration of triplets becomes unimportant. Hence, the lamellar phase is stable for nearly symmetric diblocks, despite the absence of triplets, because it is favored by the quartic terms.

III. THE *Fddd* PHASE

Experimental scattering results of Bates and co-workers for ISO and CE$_E$E triblock indicate the existence of a stable *Fddd* phase in which the {111}, {022}, and {004} peaks nearly coincide in powder pattern scattering [6,7]. Exact coincidence of the magnitudes of these three sets of reciprocal lattice vectors would occur for a unit cell in which the lengths of the orthorhombic unit cell along three orthogonal axes have ratios

$$a{:}b{:}c = 1{:}2{:}2\sqrt{3}. \qquad (5)$$

The numerical SCFT results of Tyler and Morse with a unit cell of adjustable dimensions find ratios of unit cell dimensions that differ very little from these values in simulations of both ISO triblocks and of weakly segregated diblocks.

To construct a Landau theory of the *Fddd* phase, we thus consider a single-wave-number approximation in which the primary set of reflections includes the 14 wave vectors in the {111}, {022}, and {004} families, all of which are assumed to have magnitude $|\mathbf{G}| = q^*$, and in which the unit cell dimensions are thus assumed to exactly satisfy Eq. (5).

As noted above, the stable crystal structures in the Landau theory tend to be those in which there exists a primary set of wave vectors with $|\mathbf{G}| = q^*$, among which there exist triplets of wave vectors that satisfy Eq. (4). In the *Fddd* phase, the condition $|\mathbf{G}| = q^*$ is satisfied by the choice of a special set of unit cell dimensions. In addition, this structure is found to contain two different families of triplets among the primary wave vectors. There are four triplets of the form $(11\bar{1})$, $(\bar{1}1\bar{1})$, $(0\bar{2}2)$, and two of the form (022), $(0\bar{2}2)$, $(00\bar{4})$. The *Fddd* phase thus satisfies both of the conditions for a plausible candidate phase in the Landau theory, despite the fact that the magnitudes of the primary wave vectors are not guaranteed to be equal by symmetry, and that the existence of triplets that satisfy Eq. (4) is not guaranteed by the existence of a threefold axis, as is the case for both BCC and Hex phases.

In order to describe a crystal with a specified space group symmetry the order parameter field $\psi(\mathbf{r})$ may, in general, be expanded in terms of symmetry-adapted basis functions, as a sum

$$\psi(\mathbf{r}) = \sum_i \Psi_i \phi_i(\mathbf{r}), \qquad (6)$$

where each basis function $\phi_i(\mathbf{r})$ has the specified space group symmetry. Each such basis function may be constructed as a sum

$$\phi_i(\mathbf{r}) = \frac{1}{\sqrt{n_i/2}} \sum_{a=1}^{n_i} c_a \exp(i\mathbf{G}_a \cdot \mathbf{r}) \tag{7}$$

of a family of plane waves that are related by symmetry. Here, n_i is the number of reciprocal lattice vectors used to construct the ith such basis function. For centrosymmetric groups, the coefficients c_as are real, and their values are ±1. The normalization follows Leibler's convention.

In a single-wave-number approximation, we include only the term or terms in expansion (6) corresponding to the primary wave vectors of the crystal. In the bcc, hexagonal, and lamellar phase, the Fourier amplitudes associated with the primary wave vectors are related by the assumed space group symmetries of these phases. The order parameter field $\psi(\mathbf{r})$ for each of these phases may thus be approximated as a product $\psi(\mathbf{r}) \simeq \Psi\phi(\mathbf{r})$, in which $\phi(\mathbf{r})$ is a single basis function constructed from the primary wave vectors, and Ψ is a single scalar order parameter.

In a single-wave-number approximation for an *Fddd* crystal, however, the assumed space group symmetry does not impose any relationship between the magnitudes of Fourier components $\psi_{\mathbf{G}}$ associated with the {111}, {220}, and {004} families of primary wave vectors. Our description of the *Fddd* phase is thus based upon an approximation for $\psi(\mathbf{r})$ as a sum

$$\psi(\mathbf{r}) \simeq \Psi_1\phi_1(\mathbf{r}) + \Psi_2\phi_2(\mathbf{r}) + \Psi_3\phi_3(\mathbf{r}) \tag{8}$$

in which three order parameters Ψ_1, Ψ_2, Ψ_3 and three corresponding basis functions are used to specify separately the magnitudes of the {111}, {022}, and {004} families of wave vectors, with a correspondence:

$$\phi_1(\mathbf{r}) \leftrightarrow \{111\},$$

$$\phi_2(\mathbf{r}) \leftrightarrow \{022\},$$

$$\phi_3(\mathbf{r}) \leftrightarrow \{004\}. \tag{9}$$

These basis functions are constructed using the convention of Eq. (7), in which we take $c_a=1$ for the wave vectors (111), (022), and (004) and their inverses, $(\bar{1}\bar{1}\bar{1})$, $(0\bar{2}\bar{2})$, and $(00\bar{4})$. Imposition of the *Fddd* space group symmetry then yields values $c_a=-1$ for all of remaining eight primary wave vectors in the three basis functions.

IV. SIMPLIFIED LANDAU THEORY

Alexander and McTague considered a simplified form of a Landau theory in which any wave-vector dependence of the cubic and quartic coefficients is ignored. The free energy of a crystal in this theory may be expressed as

$$f = \frac{V}{2}\sum_{\mathbf{G}} \Gamma^{(2)}(\mathbf{G})\psi_{\mathbf{G}}^2 + \int d\mathbf{r}\left[\frac{\gamma}{3!}\psi^3(\mathbf{r}) + \frac{\lambda}{4!}\psi^4(\mathbf{r})\right]. \tag{10}$$

This approximation may be obtained by approximating $\Gamma^{(3)}(\mathbf{G}_1,\mathbf{G}_2,\mathbf{G}_3)$ by a constant γ for all triplets of wave vectors that satisfy Eq. (4), and approximating $\Gamma^{(4)}(\mathbf{G}_1,\mathbf{G}_2,\mathbf{G}_3,\mathbf{G}_4)$ for all sets of four wave vectors for which $\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_3+\mathbf{G}_4=0$, by a constant λ. In a single-wave-number approximation, we may replace the second-order coefficient $\Gamma^{(2)}(|\mathbf{G}|)$ by its minimum value $\tau=\Gamma^{(2)}(q^*)$, and associate the cubic coefficient γ in this theory with the value $\gamma=\Gamma^{(3)}(\mathbf{G}_1,\mathbf{G}_2,\mathbf{G}_3)$ obtained for any triplet of wave vectors that satisfy Eq. (4), without any further loss of generality. There is, however, a further approximation introduced by approximating the function $\Gamma^{(4)}(\mathbf{G}_1,\mathbf{G}_2,\mathbf{G}_3,\mathbf{G}_4)$ by a constant λ.

The free energy densities $f=\Gamma/V$ of the BCC, hexagonal, and lamellar phases, which may be expressed as functions of a single scalar order parameter Ψ, are

$$f_{\text{lam}} = \tau\Psi^2 + \tfrac{1}{4}\lambda\Psi^4, \tag{11}$$

$$f_{\text{hex}} = \tau\Psi^2 - \frac{2}{3\sqrt{3}}\gamma\Psi^3 + \frac{5}{12}\lambda\Psi^4, \tag{12}$$

$$f_{\text{bcc}} = \tau\Psi^2 - \frac{4}{3\sqrt{6}}\gamma\Psi^3 + \frac{5}{8}\lambda\Psi^4. \tag{13}$$

The numerical coefficient of the cubic term in each of the above expressions is given by $m/(n/2)^{3/2}$, where m is the number of distinct triplets of primary wave vectors $\mathbf{G}_1+\mathbf{G}_2+\mathbf{G}_3=0$, and n is the number of primary wave vectors (i.e., $n=12$ and $m=8$ for BCC and $n=6$ and $m=2$ for hex). The free energy density of the *Fddd* phase is found to be

$$\begin{aligned} f_{Fddd} = {} & \tau(\Psi_1^2+\Psi_2^2+\Psi_3^2) - \gamma\left(\frac{1}{\sqrt{2}}\Psi_1^2\Psi_2 + \Psi_2^2\Psi_3\right) \\ & + \lambda\left(\frac{5}{16}\Psi_1^4 + \frac{3}{8}\Psi_2^4 + \frac{1}{4}\Psi_3^4 + \Psi_1^2\Psi_2^2 + \Psi_2^2\Psi_3^2 + \Psi_1^2\Psi_3^2 \right. \\ & \left. + \frac{1}{\sqrt{2}}\Psi_1^2\Psi_2\Psi_3\right). \end{aligned} \tag{14}$$

In each case, the free energy must be obtained by minimizing with respect to the order parameters.

A crude variational approximation for the free energy of the *Fddd* phase may be obtained by arbitrarily assuming that the Fourier coefficient of all 14 primary wave vectors are of equal absolute magnitude. This allows a description in terms of a single order-parameter Ψ analogous to that used for the Lam, Hex, and BCC phases, with $\Psi_1=\Psi\sqrt{4/7}$, $\Psi_2=\Psi\sqrt{2/7}$, $\Psi_3=\Psi\sqrt{1/7}$. This yields a free energy density

$$f_{Fddd} = \tau\Psi^2 - \frac{6}{7\sqrt{7}}\gamma\Psi^3 + \frac{99}{196}\lambda\Psi^4 \tag{15}$$

in which the cubic coefficient is given by $m/(n/2)^{3/2}$ for a structure with $m=6$ triplets and $n=14$ wave vectors.

The free energy density for each of the above phases may be expressed in a nondimensional form by defining dimensionless variables

$$\hat{\Psi}_i = \frac{\Psi_i}{\Psi^*}; \quad \hat{\tau} = \frac{\tau}{\tau^*}; \quad \hat{f} = \frac{f}{f^*} \tag{16}$$

in which

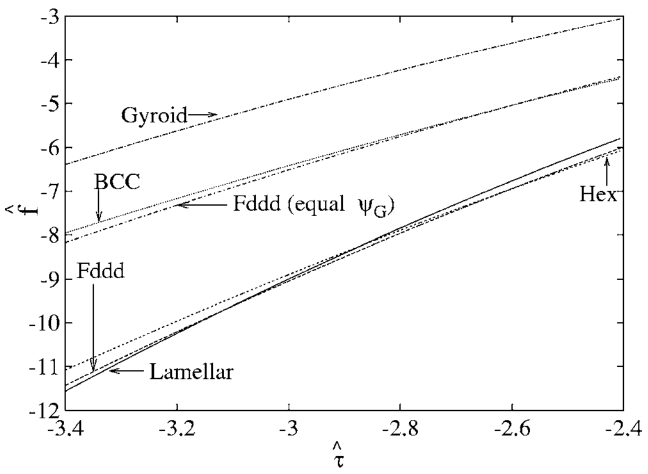

FIG. 1. Nondimensionalized Landau free energy $\hat{f}$ vs nondimensionalized temperature $\hat{\tau}$ for various competing phases in one wave-number approximation. The line labeled "*Fddd* (equal ψ_G)" is the approximation for the *Fddd* free energy in which all primary wave vectors have Fourier amplitudes of equal magnitude, as in Eq. (15).

$$\Psi^* = \frac{\gamma}{\lambda}; \quad \tau^* = \frac{\gamma^2}{\lambda}; \quad f^* = \frac{\gamma^4}{\lambda^3} \qquad (17)$$

to obtain dimensionless free energy densities of the form

$$\hat{f} = \hat{\tau}\sum_i \hat{\Psi}_i^2 + \sum_{i,j,k} \alpha_{ijk}\hat{\Psi}_i\hat{\Psi}_j\hat{\Psi}_k + \sum_{i,j,k,l} \beta_{ijkl}\hat{\Psi}_i\hat{\Psi}_j\hat{\Psi}_k\hat{\Psi}_l \qquad (18)$$

for each phase. Here, the indices i, j, k, and l run from 1 to 3 in the *Fddd* phase, but take on only a single value (and are thus unnecessary) in the other three phases. The coefficients α_{ijk} and β_{ijkl} are the numerical coefficients that appear as prefactors of γ and λ in Eqs. (11)–(15).

The minimum in the dimensionless free energy $\hat{f}$ of the *Fddd* phase with respect to the three-order parameters of the *Fddd* phase, or the single-order parameter of any of the other phases, is a function of $\hat{\tau}$, and of the coefficients α_{ijk}, and β_{ijkl}. For two phases μ and ν, the phase boundary is obtained by equating the minimized free energies and solving for $\hat{\tau}$. The phase boundary between two phases may thus be characterized by a dimensionless number $\hat{\tau}_{\mu\nu}$. The value of τ at the phase boundary depends quadratically upon γ, as seen from Eqs. (16) and (17).

Nondimensionalized free energy curves for the candidate phases as functions of $\hat{\tau}$ are shown in Fig. 1. A comparison of the *Fddd* free energy curves which correspond to the cases of (a) equal Fourier amplitudes of Eq. (15), and (b) unequal order parameters, emphasizes the importance of consideration of *three* order parameters. The region of the intersection of the BCC and hexagonal free energy curves is not included in the figure. The gyroid phase is not stable within a single-wave-number approximation at any temperature. The *Fddd* network is, however, stable within a narrow window between the Hex and lamellar phase. The nondimensional equilibrium transition temperatures are: $\hat{\tau}_{bcc-Hex} \approx -0.075$, $\hat{\tau}_{Hex-Fddd} \approx -2.61$, and $\hat{\tau}_{fddd-lam} \approx -3.12$. At $\hat{\tau} = -2.87$, which corresponds to the metastable lamellar-hexagonal phase boundary, the dimensionless order parameters in the stable *Fddd* phase are $(\Psi_1, \Psi_2, \Psi_3) \approx (2.135, 0.82, -0.4)$. The ratios of the magnitudes of the corresponding Fourier amplitudes that appear in Eq. (1) are $(|\psi_{111}|:|\psi_{022}|:|\psi_{004}|) = (7.118:2.256:1)$. The nondimensional free energy for the *Fddd* phase at this $\hat{\tau}$ is $\hat{f} = -8.332$.

At the same value of $\hat{\tau} = -2.87$ the free energy surface for the *Fddd* phase given by Eq. (18) is found to have two additional local minima at the coordinates $(0, 0, -2.39)$ and $(0, 1.824, 1.29)$ with a nondimensional free energy value of -8.237. They, respectively, correspond to lamellar and Hex phases. In addition to these local minima, we have also found saddle points at $(0, 1.258, -0.89)$, $(1.2, 0.45, -1.61)$, and $(1.196, 1.58, 0.395)$. The first of these saddles lies in the Ψ_2-Ψ_3 plane that contains lamellar and Hex phases and has the free energy value of -3.057. The second and third saddles lie close to the lines joining the lamellar and the *Fddd*, and the Hex and the *Fddd* minima, and have free energy values of -6.505 and -6.131, respectively. These values yield energy barriers of magnitudes 2.106 and 1.827 for lamellar-*Fddd* and *Fddd*-Hex transitions, respectively, but a much larger barrier value of 5.18 for direct lamellar-hexagonal transition. This suggests that a transition from lamellar to hexagonal phases that passes through *Fddd* structure could be more facile than a direct lamellar-hexagonal transition.

V. DIBLOCK COPOLYMERS: EXTENDING LEIBLER'S THEORY

In this section we present an extension of Leibler's theory of weakly segregated diblock copolymers, in which we allow for the appearance of a *Fddd* phase. Following Leibler's approach, we use wave-vector-dependent coefficients in the Landau expansion with values that are calculated from polymer self-consistent-field theory.

The self-consistent-field free energy functional may be expressed as the sum of an *ideal gas* part and a part arising out of interaction:

$$F[\langle\rho_\alpha\rangle] = F_{\text{ideal}}[\langle\rho_\alpha\rangle] + F_{\text{int}}[\langle\rho_\alpha\rangle], \qquad (19)$$

where ρ_α is the concentration of individual monomers α ($\alpha = \{A, B\}$), and the interaction part is assumed to be local. The interaction free energy has the form $v\int d\mathbf{r}\, \chi\rho_A(\mathbf{r})\rho_B(\mathbf{r})$, where χ is the Flory-Huggins interaction parameter and v is a corresponding monomer reference volume. In an incompressible liquid of diblock copolymers, we may use an order parameter $\psi(\mathbf{r}) = v\langle\delta\rho_A(\mathbf{r})\rangle = -v\langle\delta\rho_B(\mathbf{r})\rangle$. The free energy expansion in Ψ_i's is of the form as in Eq. (2) with $\mathbf{G}_1 + \cdots + \mathbf{G}_n = 0$ in all the terms in the expansion.

Because the interaction term in Eq. (19) is quadratic in the density, only the second-order term depends upon the interaction parameter χ, while all higher-order terms may be calculated from correlation functions of ideal Gaussian chains. The second-order coefficient $\Gamma^{(2)}$ has a minimum at a wave vector $q^* \propto 1/R_g$, and has a value $\tau = 2(\chi_s - \chi)$ for $q = q^*$. Expressions for the cubic and quartic coefficients are given by

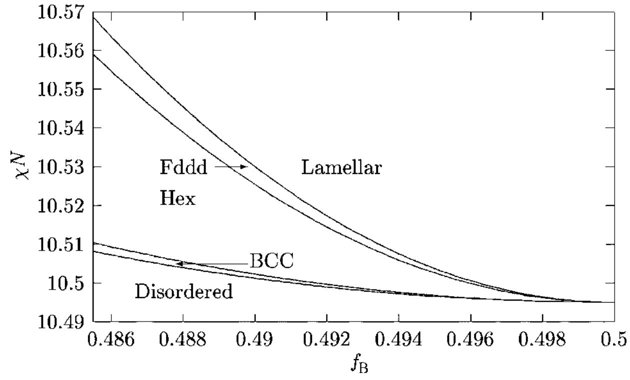

FIG. 2. The phase diagram for weakly segregated diblock copolymers calculated using a simplified Landau theory analogous to that of Alexander and McTague.

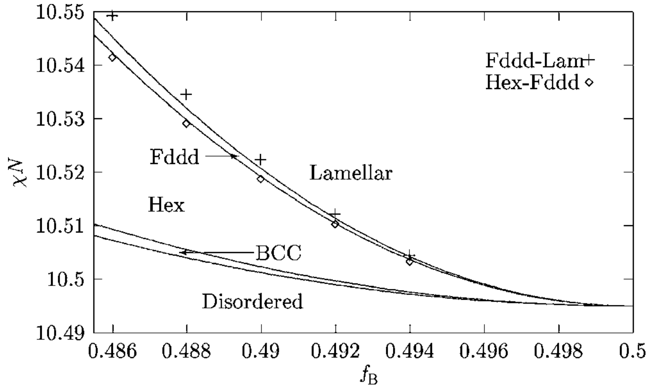

FIG. 3. The phase diagram of weakly segregated diblock copolymers calculated using an extension of Leibler's theory. Full lines are the phase boundaries calculated from the Landau theory. Points denoted by + are the lamellar-*Fddd* boundary points and ◇ are the *Fddd*-hexagonal boundary points calculated using the numerical SCFT method.

Leibler [2], as are expressions for the free energies for the lamellar, hexagonal, and bcc phases. The free energy density of the *Fddd* phase is

$$\begin{aligned} v f_{Fddd} &= 2(\chi_s-\chi)({\Psi_1}^2+{\Psi_2}^2+{\Psi_3}^2)+\Gamma^{(3)}\left(\frac{{\Psi_1}^2\Psi_2}{\sqrt{2}} + {\Psi_2}^2\Psi_3\right) + \frac{{\Psi_1}^4}{16}\left[\Gamma^{(4)}(0,0)+\Gamma^{(4)}\left(0,\frac{1}{4}\right)\right. \\ &\quad \left. + 4\Gamma^{(4)}\left(0,\frac{3}{4}\right)+\Gamma^{(4)}(0,1)-2\Gamma^{(4)}\left(\frac{1}{4},\frac{3}{4}\right)\right] + \frac{{\Psi_2}^4}{8} \\ &\quad \times[\Gamma^{(4)}(0,0)+2\Gamma^{(4)}(0,1)] + \frac{{\Psi_3}^4}{4}\Gamma^{(4)}(0,0)+\frac{{\Psi_1}^2{\Psi_2}^2}{2} \\ &\quad \times\left[\Gamma^{(4)}(0,1)+\Gamma^{(4)}\left(0,\frac{3}{2}\right)\right]+{\Psi_2}^2{\Psi_3}^2\Gamma^{(4)}(0,1) \\ &\quad +{\Psi_1}^2{\Psi_3}^2\Gamma^{(4)}\left(0,\frac{3}{2}\right)+\frac{{\Psi_1}^2\Psi_2\Psi_3}{\sqrt{2}}\Gamma^{(4)}(0,1). \end{aligned} \qquad (20)$$

The arguments of $\Gamma^{(4)}$s follow the Leibler's notation and uniquely relate to the relative orientations of a *quartet* of wave vectors. The free energy of the *Fddd* phase at a given value of χN and f must be obtained by minimizing the above with respect to the three-order parameters.

One simple approximation to the phase diagram may be obtained by combining Leibler's calculation of the Landau coefficients with the simplified theory of the previous section. The coefficient $\Gamma^{(3)}$ vanishes when f_B, the volume fraction of monomer B (or A), equals to $\frac{1}{2}$, by symmetry, and varies nearly linearly with f_B, while values of $\Gamma^{(4)}$ are nearly independent of f_B near this point. The values of τ at the transitions are proportional to $(\Gamma^{(3)})^2/\Gamma^{(4)}$ in the simplified Landau theory. Correspondingly, the values of χN along each phase boundary in Leibler's theory vary nearly quadratically with f_B about $f_B=\frac{1}{2}$. In Fig. 2, we show a phase diagram calculated using the simplified Landau theory by calculating the phase boundaries at $f_B=0.496$ using Leibler's results for the coefficients at this value of f_B, while taking $\lambda=\Gamma^{(4)}(0,0)$, and assuming the value of χN at each phase boundary to vary quadratically with f_B with a minimum value of $\chi N=10.495$ at $f_B=0.5$.

The phase diagram calculated using the extended Leibler free energy represented in Eq. (20), with the wave-vector-dependent quartic term, is presented in Fig. 3, where the results are compared to the results of numerical SCFT. Within the very weakly segregated regime considered here, the agreement between the two methods is quite good, as expected. In the results shown in this figure, we have actually gone slightly beyond the approximation used in Leibler's theory by treating the common magnitude q of the primary wave vectors as an adjustable parameter, rather than setting $q=q^*$, and minimizing the free energy of each phase with respect to q as well as with respect to the order parameter(s). Allowing a variation in the primary wave number and including the wave vector dependence of the quartic coefficient slightly improve the level of agreement between the Landau theory and numerical SCFT results. Overall, however, the results of this extended Leibler theory are quite similar to those obtained with a simpler Alexander-McTague theory.

VI. DISCUSSION

The Landau theory has been used to analyze the stability of the *Fddd* structure with a special unit cell in a weakly ordered system. The structure is found to be stable in a narrow window between the hexagonal and lamellar phase. The reasons for its predicted stability in the weak segregation limit can be analyzed within the context of the Alexander-McTague theory, and seem to have more to do with geometry than with any specific feature of block copolymer self-assembly. *ABC* triblock copolymers have thus far been observed to form an *Fddd* phase only in relatively weakly segregated melts, and so the weak segregation physics described here may play an important role in stabilizing this phase in the systems in which it has thus far been observed. This raises the question of whether the phase will remain stable in more strongly segregated *ABC* triblock melts.

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