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Absence of the nematic phase in symmetric diblock copolymers

David C. Morse and Scott T. Milner
Exxon Research and Engineering, Annandale, New Jersey 08801

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We examine the possibility of nematic order in systems described by the Brazovskii model [Sov. Phys. JETP **41**, 85 (1975)] of the isotropic-lamellar phase transition, including symmetric diblock copolymer melts and bilayer-forming surfactant systems. We introduce a nematic order parameter and look for states that break rotational symmetry—that is, which have a well-defined direction for interfacial normals, but no phase coherence between interfaces. We find an isotropic-nematic phase transition, but it is always precluded by an isotropic-lamellar phase transition occurring at higher temperature. We show that the lamellar phase is stable to dislocation-mediated melting to a nematic phase in the limit of long copolymer chains, even though the isotropic-lamellar phase transition becomes second order in this limit.

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I. INTRODUCTION

The self-assembly of molecules into layers, and then into various ordered phases including lamellar or smectic phases, is well established in systems including diblock copolymers [1] and surfactant systems with vanishing spontaneous curvature [2]. In each case, interfaces arise spontaneously from repulsive interactions between different parts of a molecule more or less mixed in the isotropic phase, and microscopically separated in the ordered phases.

In these interface-forming systems, the possibility has been suggested theoretically [3], but never observed experimentally, that a self-assembled nematic phase might exist. In such a phase, orientational symmetry would be broken by selection of a layer normal direction, but translational symmetry would remain. That is, the layers would lack quasi-long-range order with regard to their vertical displacement from some reference plane.

A nematic phase may also be described in terms of the melting of an ordered smectic phase by the proliferation of dislocation lines. Detailed theory of the smectic-nematic transition [4] is in agreement with the basic criterion of Helfrich [5], in which dislocations appear when their free energy per unit persistence length becomes of order $k_B T$. Then the configurational entropy of the dislocation line is comparable to the free energy of the elastic distortion caused by the dislocation.

Besides the logical possibility of the existence of the nematic phase, we may describe the plausibility of a nematic phase as a different compromise between the elastic energy of the interfaces in a microphase-separated system and the configurational entropy; breaking rotational symmetry, by choosing a common direction in which the layer normals tend to point, reduces, e.g., the bending energy of the interfaces, while maintaining at least some configurational entropy. From the low-temperature point of view, a nematic phase is plausible if the elastic constants describing the ordered phase are weak, so that the strain energy per unit persistence length of dislocations is small compared to $k_B T$ [5].

We shall show, however, that for systems undergoing microphase separation described by the Brazovskii model, the isotropic-nematic (IN) transition exists but is always preempted by the isotropic-smectic (IS) transition. Thus, no nematic phase can appear in symmetric diblock copolymer melts of sufficiently long chains, where the Brazovskii model has been shown to be well controlled [6]. The sponge-lamellar transition in self-assembling surfactant systems has been described in terms of a Brazovskii model as well [7]; if this description is appropriate, no nematic phases are expected in surfactant-bilayer systems.

In Sec. V of this paper, we examine the Helfrich criterion for dislocation-mediated melting of copolymer lamellar phases. We find that even though the IS transition becomes second order in the limit of long chain length ($N \rightarrow \infty$), and thus the smectic elastic constants vanish, the persistence length of the dislocation lines diverges like the layer spacing; as a result, the strain energy per persistence length of a dislocation diverges in the limit of long chains. Consistent with this, we show that the effect of Landau-Peierls fluctuations on the higher-order Bragg peaks in the ordered state becomes weak in the limit of long chains, so that the order just below the transition becomes stronger as $N \rightarrow \infty$.

II. BRAZOVSKII MODEL

To describe the spontaneous microphase separation of a scalar order parameter, we consider a model Hamiltonian

$$H=\frac{1}{2}\int_q [\tau+(q-q_0)^2]\psi(q)\psi(-q)-\int_q h(q)\psi(-q)+\frac{1}{4!}\int_{q_1}\int_{q_2}\int_{q_3}\lambda(\{q_i\})\psi(q_1)\psi(q_2)\psi(q_3)\psi(-q_1-q_2-q_3)$$

where we have adopted the shorthand $\int_q \equiv \int d^3q/(2\pi)^3$ and $\{q_i\}=\{q_1, q_2, q_3, -q_1-q_2-q_3\}$. This is a generalization of the model introduced by Brazovskii [8], in which $\lambda(\{q_i\})$ is replaced by a constant λ. In an *A*-*B* diblock copolymer melt, the scalar order parameter $\psi(x)$ represents the local monomer concentration,

$$\psi(x)=\rho_A(x)-f \ ,$$

where $\rho_A(x)$ is the local volume fraction of monomer *A* and f is its average value. In surfactant systems ψ represents the volume fraction of solvent "inside" versus "outside" the bilayer. The conjugate field $h(x)$ is included to facilitate discussion of states with nonzero $\langle \psi(x) \rangle$. The effective Hamiltonian of Eq. (1) has been justified by systematic calculation using the random-phase approximation in the case of block copolymers [6], and shown to be quantitative in describing the microphase separation transition in experiment [1].

The quadratic term in Eq. (1) describes the selection of a wave number q_0 for condensation of the order parameter, without preference as to the condensation direction; τ is the reduced temperature $(T-T_c^{\rm MF})/T_c^{\rm MF}$ in mean field. Only even terms is ψ are permitted by symmetry (i.e., we consider symmetric diblock copolymers, and in the surfactant systems we may interchange the definitions of the "inside" and "outside" volumes [7]). The quartic term provides a stabilizing nonlinearity.

The ordering transition in the Brazovskii model cannot be a second-order continuous transition, because under this assumption the fluctuations in the order parameter itself diverge as the hypothetical transition temperature $\tau=0$ is approached:

$$\langle \psi^2(x) \rangle = \int_q [\tau+(q-q_0)^2]^{-1} \simeq \frac{q_0^2}{2\pi\sqrt{\tau}} \ . \tag{2}$$

The assumption of independent Gaussian fluctuations of the condensing order parameter in the entire spherical shell of directions of condensation leads to the divergence; therefore, the stabilizing quartic terms is essential to describe the transition. Or, we may say that the competition between fluctuations with wave vectors in different direction is crucial.

Brazovskii showed that a self-consistent treatment of the leading divergences as the mean-field critical temperature is approached ($\tau \to 0$) leads to a fluctuation-driven first-order phase transition at a suppressed temperature. We shall cast his approximation in a particularly transparent form, useful when we consider more complicated symmetry breaking. The treatment of Ref. [8] turns out to be equivalent to the use of the Feynman-Hellman theorem [9] which provides an upper bound on the free energy of a system in terms of an approximate partition function:

$$F < F_{\rm var} = \langle H \rangle_0 - TS_0 \tag{3}$$

with an entropy S_0 defined by

$$\begin{aligned} F_0 &\equiv -\ln \left[\int D\psi \exp(-H_0[\psi]) \right] \\ &\equiv \langle H_0 \rangle_0 - TS_0 \ . \end{aligned} \tag{4}$$

Here $\langle \ \rangle_0$ represents averages in the ensemble with Boltzmann weights given by $\exp(-H_0)$, and H_0 should be chosen, within some variational class, so as to minimize $F_{\rm var}$. To discuss the free energy as a function of the mean value of the order parameter $\langle \psi(q) \rangle$, rather than of the conjugate field $h(q)$, we introduce a corresponding Gibbs free energy

$$\Gamma(\langle \psi \rangle) \equiv F_{\rm var}[h] + \int_q h(-q) \langle \psi(q) \rangle \ .$$

The variational form for the effective Hamiltonian we take is a general quadratic form,

$$H_0 = \tfrac{1}{2} \int_q [r(q)+(q-q_0)^2] |\psi(q)-\bar\psi(q)|^2 \ , \tag{5}$$

in which $r(q)$ and $\bar\psi(q)=\langle \psi(q) \rangle_0$ are introduced as parameters. The corresponding fluctuations of the order parameter are described by a correlation function

$$\begin{aligned} G(q) &= \langle \delta\psi(q) \delta\psi(-q) \rangle_0 \\ &= [r(q)+(q-q_0)^2]^{-1} \ , \end{aligned} \tag{6}$$

where $\delta\psi(q)=\psi(q)-\bar\psi(q)$. With this form, we obtain

$$\begin{aligned} \Gamma[\bar\psi] = {} & \tfrac{1}{2} \int_q [\tau+(q-q_0)^2][G(q)+\bar\psi(q)\bar\psi(-q)] + \tfrac{1}{8} \int_{q_1} \int_{q_2} \lambda(q_1,-q_1,q_2,-q_2)[G(q_1)+2\bar\psi(q_1)\bar\psi(-q_1)]G(q_2) \\ & + \tfrac{1}{4!} \int_{q_1} \int_{q_2} \int_{q_3} \lambda(\{q_i\}) \bar\psi(q_1) \bar\psi(q_2) \bar\psi(q_3) \bar\psi(-q_1-q_2-q_3) - TS_0 \ , \end{aligned} \tag{7}$$

where

$$-TS_0 = -\tfrac{1}{2} \int_q \ln G(q) - \langle H_0 \rangle_0 \tag{8}$$

and where $\langle H_0 \rangle_0 = $const.

We may compute a bound on the free energy by minimizing Γ with respect to $r(q)$ and the mean order parameter $\bar\psi(q)$. Minimizing with respect to $r(q)$ leads to a self-consistent equation for the inverse correlation function,

$$\begin{aligned} r(q) = \tau + \tfrac{1}{2} \int_{q_1} & \lambda(q,-q,q_1,-q_1) \\ & \times [G(q_1)+\bar\psi(q_1)\bar\psi(-q_1)] \ . \end{aligned} \tag{9}$$

Differentiation of Γ with respect to $\bar\psi(q)$ leads to an approximation equation of state,

$$h(q)=\tau\bar{\psi}(q)+\tfrac{1}{2}\int_q \lambda(q,-q,q_1,-q_1)G(q_1)\bar{\psi}(q)+\tfrac{1}{3!}\int_{q_1}\int_{q_2}\lambda(-q,q_1,q_2,q-q_1-q_2)\bar{\psi}(q_1)\bar{\psi}(q_2)\bar{\psi}(q-q_1-q_2)\ . \tag{10}$$

Equations (9) and (10) may be interpreted as a self-consistent approximation for the correlation function and equation of state, corresponding to a certain infinite sum of perturbative diagrams. This is the class of diagrams shown by Brazovskii to be most divergent in the limit of small r. The equations given here reduce precisely to Brazovskii's equations when $\lambda(\{q_i\})$ is approximated by a q-independent constant λ. To evaluate Γ as a function of the order parameter, Brazovskii effectively reintegrated the equation of state (10). The advantage of the variational formulation presented here is that it allows a direct evaluation of the variational free energy, a feature that becomes particularly useful when considering states of more complicated structure.

For the case of smectic (i.e., lamellar) order, relevant to symmetric diblocks, we set

$$\begin{aligned}\bar{\psi}(q)&=a[\delta(q+q_0)+\delta(q-q_0)]\ ,\\ h(q)&=h[\delta(q+q_0)+\delta(q-q_0)]\ .\end{aligned} \tag{11}$$

Note that in this case $\lambda(\{q_i\})$ appears in Eqs. (9) and (10) only with arguments of the form $\lambda(q_1,-q_1,q_2,-q_2)$. Note also that the important fluctuations in this model are all at wave vectors of magnitude $q\simeq q_0$, allowing us to retain only the angular dependence of $\lambda(\{q_i\})$ and $r(q)$. We will thus approximate q with q_0 when it appears outside of the propagator $G(q)$, and approximate $\lambda(q_1,-q_1,q_2,-q_2)\rightarrow\lambda(\hat{q}_1\cdot\hat{q}_2)$ and $r(q)\rightarrow r(\hat{q})$ as functions of the unit vectors $\hat{q}_1$ and $\hat{q}_2$.

III. NEMATIC ORDER PARAMETER

To extend the model of Ref. [8] to describe nematic symmetry breaking, we introduce the following composite operator as the nematic order parameter:

$$Q_{ij}(x)=\nabla_i\psi\nabla_j\psi-\tfrac{1}{3}\delta_{ij}(\nabla\psi)^2\ . \tag{12}$$

The expectation value of this operator samples the anisotropy of the distribution of fluctuation wave vectors, or of the gradients of the original scalar order parameter. These gradients define the normal direction of interfaces arising in the fluctuations of the isotropic state. Hence Eq. (11) is a natural choice to study orientational symmetry breaking.

We are interested in symmetry breaking with this order parameter at long wavelength, so we concentrate on the uniform component of Q_{ij}. We can, without loss of generality, focus on the appearance of uniaxial order aligned along the $\hat{\mathbf{z}}$ axis, which we describe with a related scalar order parameter

$$Q\equiv\int_q Y_{20}(\hat{q})\psi(q)\psi(-q)\ , \tag{13}$$

where $Y_{20}(\hat{q})$ is the $l=2$, $m=0$ spherical harmonic. The order parameter $\psi(q)$ has significant fluctuations only for wave vectors of magnitude $|q|\simeq{}_0$, so that $q_0^2Q\propto Q_{zz}$. In order to study fluctuations and possible ordering of Q, we introduce a field τ_2 conjugate to $\frac{1}{2}Q$, so that $H\rightarrow H-\frac{1}{2}\tau_2 Q$. The field τ_2 has the interpretation of an anisotropic mean-field susceptibility; it favors the condensation of ψ in a particular direction.

We may now proceed in several ways. To begin with, we can identify a self-consistent equation that sums the set of most-divergent programs for quantities such as the susceptibility to the anisotropic field τ_2. This susceptibility, equivalent to the correlation function for nematic fluctuations, is defined by

$$S_{QQ}\equiv\left.\frac{\partial^2 F}{\partial\tau_2\partial\tau_2}\right|_{\tau_2=0}\ . \tag{14}$$

A divergence is this susceptibility determines the nematic spinodal, the limit of stability of the isotropic phase to nematic fluctuations. Formal summation of the set of diagrams shown in Fig. 1 gives a Dyson equation

$$S_{QQ}=\frac{\Pi}{1+\lambda_2\Pi}\ , \tag{15}$$

where

$$\Pi=\tfrac{1}{2}\int_q|Y_{20}(\hat{q})|^2G^2(q)\simeq\frac{q_0^2}{8\pi r^{3/2}} \tag{16}$$

is the one-loop nematic susceptibility and λ_2 is the $l=2$ component of $\lambda(\hat{q}_1,\hat{q}_2)$, defined via the decomposition

$$\lambda(q_1,-q_1,q_2,-q_2)=\sum_{l,m}Y_{lm}^*(\hat{q}_1)Y_{lm}(\hat{q}_2)\lambda_l\ . \tag{17}$$

Only even values of l contribute to the sum in Eq. (17), since λ must be even under $q_1\rightarrow q_1$. In what follows, we will retain only the $l=0$ and $l=2$ components of λ, giving an explicit form $4\pi\lambda(\hat{q}_1\cdot\hat{q}_2)=\lambda_0+\frac{5}{2}[3(\hat{q}_1\cdot\hat{q}_2)^2-1]\lambda_2$.

We retain the wave-vector dependence of λ because it is evident from Eq. (15) that if λ is independent of $\{q_i\}$, then S_{QQ} is unrenormalized by the quartic interactions. It is also evident that a divergence of S_{QQ} can occur only when λ_2 is negative. A negative value of λ_2 results in a smaller quartic interaction for fluctuations with parallel wave vectors than for perpendicular wave vectors, which naturally favors nematic alignment. Note that the quartic coupling resulting from the calculations of Ref. [6] is indeed anisotropic; in the copolymer system the interaction is obviously nonlocal, since the polymer chains are extended objects. There is a limit to how anisotropic the quartic coupling can be, since the theory must be stabilized by the quartic coupling at high temperatures; for a

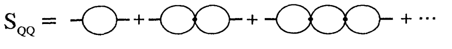

FIG. 1. Class of diagrams contributing to the nematic susceptibility S_{QQ}.

single large-amplitude fluctuation to be stable we require that $\lambda_0+5\lambda_2>0$. The basic mechanism in the Brazovskii calculation for shifting the transition temperature and altering the shape of the effective potential is contained in the "feedback" from the correction to the reduced temperature arising from the quartic nonlinearity, expressed in Eq. (9). The analogous mechanism for the nematic fluctuations is expressed in Eq. (15).

It is now straightforward to estimate the importance of nematic and smectic fluctuations in the isotropic state by calculating two Ginzburg criteria [10]—one for smectic fluctuations arising from Eq. (7) and one for nematic fluctuations arising from Eq. (15). These criteria estimate the temperature at which the first perturbative correction is of the same order as the bare susceptibility. For the lamellar susceptibility of Eq. (7), this is

$$\lambda_0\int_q G_0(q)\sim\tau,\quad \tau\sim(\lambda_0 q_0^2)^{2/3}\ , \tag{18}$$

where $G_0(q)\equiv[\tau+(q-q_0)^2]^{-1}$ is the mean-field correlation function. For the nematic susceptibility of Eq. (15), the corresponding Ginzburg criterion is

$$\lambda_2\int_q |y_{20}(\hat{q})|^2 G_0^2(q)\sim 1,\quad \tau\sim(\lambda_2 q_0^2)^{2/3}\ . \tag{19}$$

We find that the two Ginzburg temperatures are of the same order for an anisotropy of the quartic term of relative order unity. A more detailed calculation is required to determine whether the smectic phase is ever preempted by a transition to a nematic phase.

IV. STABILITY OF THE ISOTROPIC PHASE

We expect, based on standard symmetry arguments [11], that an IN transition should be first order, and should occur at a temperature above the stability threshold given in Eq. (15). Rather than attempting to discover the set of diagrams for the free energy, we may employ the variational approach of Sec. II. A variational description of a nematic phase is obtained by setting $\bar{\psi}(-q)=0$ but letting $r(q)$ be anisotropic. We shall compute the variational free energy for a nematic phase in an approximation analogous to the original Brazovskii approximation, but in the presence of an external field τ_2. By expanding this energy in powers of τ_2, we can recover the susceptibility of Eq. (15).

It is useful first to decompose the angular dependence of r and τ in spherical harmonics,

$$\begin{aligned} r_l&=\int d^2\hat{q}\ Y_{l0}^*(\hat{q})r(\hat{q})\ ,\\ \tau_l&=\int d^2\hat{q}\ Y_{l0}^*(\hat{q})\tau(\hat{q})\ , \end{aligned} \tag{20a}$$

and similarly to decompose the "bubble" integral, defining

$$\begin{aligned} q_l&=\int_q Y_{l0}^*(\hat{q})G(q)\\ &\simeq\frac{q_0^2}{8\pi^2}\int d^2\hat{q}\frac{Y_{l0}^*(\hat{q})}{\sqrt{r(\hat{q})}}\ . \end{aligned} \tag{20b}$$

In the above equations, $\int d^2\hat{q}$ refers to an integral over the unit sphere, and l is always assumed to be even. Note that, in this notation, $g_0=\langle\delta\psi^2(x)\rangle/\sqrt{4\pi}$ and $g_2=Q$.

Self-consistent equations (9) and (10) for a state with both lamellar order and anisotropic fluctuations can then be written

$$\begin{aligned} r_l&=\tau_l+\tfrac{1}{2}\lambda_l g_l+\lambda_l y_l a^2\ ,\\ h&=\sum_l(r_l y_l a-\tfrac{1}{2}\lambda_l y_l^2 a^3)\ , \end{aligned} \tag{21}$$

where $y_l\equiv Y_{l0}(\hat{\mathbf{z}})$. Similarly, the variational free energy of Eq. (7) can be written

$$\begin{aligned} \Gamma=&\sum_l(\tfrac{1}{2}\tau_l-r_l)g_l+\tfrac{1}{8}\lambda_l g_l^2)\\ &+\sum_l\{\tau_l y_l+\tfrac{1}{2}\lambda_l y_l g_l+\tfrac{1}{4}\lambda_l y_l^2 a^2\}a^2-TS_0\ , \end{aligned} \tag{22}$$

where

$$-TS_0=\frac{q_0^2}{8\pi^2}\int d\hat{q}\sqrt{r(\hat{q})}+\text{const}\ . \tag{23}$$

While these equations are valid for an arbitrary interaction λ, in practice we will consider an interaction in which $\lambda_l=0$ for $l>2$. By use of Eq. (21), this also gives an $r(\hat{q})$ with only $l=0$ and $l=2$ components, and allows the angular integrals of Eqs. (20) and (23) to be evaluated analytically.

To describe a smectic phase we can fix a and use Eq. (21) to determine r_l (or, equivalently, g_1), giving a smectic free energy $\Gamma_S(a)$. Note that, for a q-dependent quartic interaction, the presence of lamellar order generally induces some anisotropic fluctuations, or nematic order. To describe a pure nematic phase, we set $a=0$, set $g_2=Q$, and use Eq. (21) to determine g_0, giving a nematic free energy $\Gamma_N(Q)$.

We have calculated the transition temperatures τ_S and τ_N for the IS and IN transitions as a function of the ratio λ_2/λ_0 describing the anisotropy of the quartic coupling (see Fig. 2). We have considered only negative values of λ_2, since these favor nematic order. We find that although there is indeed a first-order transition to the nematic phase for $\lambda_2<0$, it is precluded by the smectic phase transition for all $\lambda_0+5\lambda_2>0$, corresponding to Hamiltonians that are stable at high temperatures. Since both transition temperatures are depressed by the same order in λ (or in $1/N$) below the mean-field transition, we know of no way of arriving at this conclusion without explicit calculation. We note that the strongly anisotropic quartic coupling that favors nematic order also favors the smectic ordering, and raises the temperature τ_S as well as τ_N.

Suppose we attempt to favor nematic phases with an explicit microscopic Maier-Saupe or Onsager-like nematic coupling [12–14] between the individual bonds in the case of diblock copolymers. This modification of the theory is ineffective in producing a nematic phase, for the following reason: The smectic ordering in diblock copolymers initially has a wavelength of the order of the radius of gyration of the polymers. The fractional deformation of the radius of gyration at temperatures near the transition is thus of order unity, while the corresponding

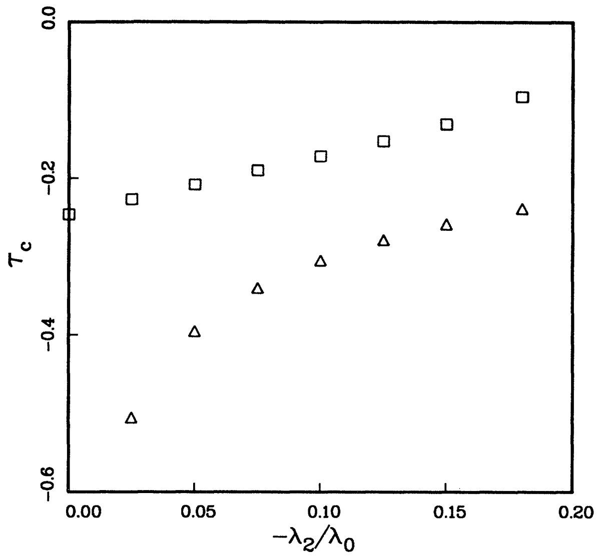

FIG. 2. Transition temperatures τ_c for the isotropic-smectic (□) and isotropic-nematic (△) transitions plotted vs the ratio $-\lambda_2/\lambda_0$ describing the anisotropy of the quartic interaction. The τ_c are measured in units of $(\lambda_0 q_0^2)^{-2/3}$.

induced bond orientational order is extremely weak, of order $1/N$. Thus there is very little opportunity for "feedback" between concentration fluctuations driven by the incompatibility of the monomers, and nematic ordering driven by the microscopic nematic coupling, until the molecules are very stiff or very short ($N \rightarrow 1$).

V. STABILITY OF THE SMECTIC PHASE

A complementary way to describe and search for a nematic phase is to consider the melting of the ordered smectic phase by the proliferation of wandering dislocations [15,5,4]. Small dislocation loops have a finite core and far-field strain free energy, and are present in thermal equilibrium in some concentration at all temperatures. These pointlike defects do not destroy the quasi-long-range order in smectics. A finite density of "unbound" dislocation lines, in contrast, destroys the quasi-long-range order on length scales large compared to the distance between such lines [4].

A simple criterion for melting by the growth of dislocation loops from small pointlike defects to wandering unbound dislocation lines was given by Helfrich [5]. The configurational entropy of the wandering dislocation line is of order $k_B T$ per persistence length l_p (the scale on which the tangent to the dislocation is decorrelated). When this entropy per unit length is of the same magnitude as the sum of the core and far-field strain free energies per unit length, the dislocation line begins to be favorable.

Because the microphase-separation transition becomes second order in the limit of $N \rightarrow \infty$ for diblock copolymers [16], the elastic constants B and K of the ordered smectic phase just below the transition $T = T_s^-$ must become indefinitely small. One might expect in this limit that the strain energies associated with a dislocation would become arbitrarily small, and so the Helfrich criterion for dislocation-mediated melting to a nematic phase would be satisfied. (Of course, if we found, using a low-temperature argument, that the smectic phase was unstable to melting to a nematic phase at $T = T_s^-$, this would contradict our high-temperature calculation.)

We shall not pursue a mapping of the copolymer system onto the detailed calculations of Ref. [4], as this would require a calculation of quantities such as the core energy for dislocations, etc. Instead, we employ a simple calculation [15] of the far-field strain energy of an edge dislocation, in terms of the harmonic elastic free-energy density of smectic phases:

$$f = \tfrac{1}{2}[B(\partial_z u)^2 + K(\nabla^2 u)^2] \; . \tag{24}$$

The contribution to the strain energy per unit length from regions farther than a layer spacing d from the dislocation core is

$$\varepsilon \sim K u_0^2/(\xi a) \; . \tag{25}$$

Here u_0 is the magnitude of the Burger vector of the dislocation (e.g., a layer spacing), a is the in-plane dimensions of the core (assumed to be of order u_0), and ξ is the smectic penetration length $\xi = (K/B)^{1/2}$. The missing coefficient in Eq. (25) depend on the separation of the strain free energy into core and far-field portions.

We require the long-wavelength smectic elastic coefficients K and B for the copolymer system just below the smectic transition. We find these by extending the calculation of the condensation free-energy change—which is, by definition, zero at the first-order transition—to condensation into a slightly distorted state. In contrast to the preceding section, we shall compute these coefficients with no anisotropy of the quartic coupling.

The distortion appropriate to determine B can be induced by condensation at a slightly unfavorable wave number, i.e., $|q| = q_0 + q_z$ with $q_z \ll q_0$. The corresponding change in the layer spacing is $\delta d/d = -\delta q/q_0 = -q_z/q_0$, which implies a layer-displacement field given by $\partial_z u = -q_z/q_0$. We calculate the amplitude of ordering and the free energy of the ordered state to order $O(q_z^2)$.

At $T = T_c^-$, the free energies of the disordered and undistorted ordered states are equal. The disordered state has zero free energy by definition, so the slightly positive free energy of the distorted ordered state is the elastic free energy. (This distorted state is only metastable at $T = T_c^-$ since it is of higher free energy than the disordered state.) Hence, the positive condensation free-energy density at $T = T_c^-$ for such a distortion is related to the smectic modulus by

$$\delta\Gamma = \tfrac{1}{2}B(\partial_z u)^2 = \tfrac{1}{2}B(q_z/q_0)^2 \; . \tag{26}$$

Similarly, to determine the bending elasticity K, we condense with a small-amplitude ripple in the layer positions, i.e., a concentration profile of the form

$$\psi(x,z)=2a\cos[q_0(z+2u_0\cos q_\perp x)],\quad q_\perp \ll q_0\ , \tag{27}$$

In this case, we calculate the amplitude of ordering and the free energy of the ordered state to order $\mathcal{O}(q_\perp^4)$. The transverse ripple in the layer displacement $u(x)=2u_0\cos q_\perp x$ implies an elastic energy density (averaged over a period) equal to the free-energy density of the rippled ordered state. Hence

$$\delta\Gamma=\tfrac{1}{2}K(\nabla_\perp^2 u)^2=Kq_\perp^4u_0^2\ . \tag{28}$$

Rotational invariance [11] determines the form of the smectic elastic free energy, Eq. (24), and of the condensation free-energy densities, Eqs. (26) and (28), which arise naturally from our calculation.

We find after a calculation of free-energy differences analogous to those presented in Sec. II that the smectic elastic constants B and K at $T=T_c^-$, just inside the ordered smectic phase, are given by

$$K=r/\lambda,\quad B=4q_0^2r/\lambda\ . \tag{29}$$

Note that the penetration length $\xi=(2q_0)^{-1}$ is of the same order as the layer spacing from Eq. (29).

We assume that the persistence length of the dislocation line is of the order of the layer spacing, which is comparable to the penetration length. This is the only small length scale in the problem, and it is hard to imagine the persistence length being shorter than this. Hence the dislocation-line strain free energy per persistence length l_p is roughly

$$\varepsilon l_p \sim K/q_0 \sim (q_0/\lambda)^{1/3}\ . \tag{30}$$

The smectic phase is thus stable whenever $\lambda \ll q_0$. We note, furthermore, that Brazovskii's approximation for the free energy is accurate [8] only when $\lambda/q_0 \ll 1$, i.e., when the transition is only weakly first order. The lamellar phase thus remains stable at temperatures up to the IS transition temperature in any system whose IS transition is well described by the Brazovskii approximation.

To describe the lamellar phase of diblock copolymers, we use the prescription given in Ref. [16] for mapping the Leibler free energy onto the Brazovskii Hamiltonian. Rescaling the concentration field by $c^2a^2\psi^2/v=\tilde{\psi}^2$, where $c^2=1.214$ for symmetric copolymers, leads to parameter $\tau=2(\chi_s-\chi)/(c^2a^2)$, $\lambda=156.56v/(Nc^4a^4)$, and $q_0^2=22.71/(Na^2)$, where the spinodal value of χ is $\chi_x=10.495/N$. Using these values, we obtain smectic constants $B=30.15a^6/v^3\bar{N}^{-4/3}$ and $K=0.332a^2/v\bar{N}^{-1/3}$, where $\bar{N}\equiv Na^6/v^2$. The elastic constants indeed vanish as $N\to\infty$, as they must when the transition becomes second order. The dislocation-line energy per persistence length, nonetheless, diverges as

$$\varepsilon l_p \sim \bar{N}^{1/6} \tag{31}$$

in the limit of long chains, due to the divergence of l_p. As a result, the smectic order becomes better and better defined with increasing N.

Another way to ask about the degree of disorder in the smectic phase is to compute the Caille exponent [17] governing the power-law tails around each quasi-Bragg peak. These tails in the scattering are the result of Landau-Peierls fluctuations [18,19], or undulation modes [11], which are transverse fluctuations of the layer positions. Near the Bragg condition the structure factor varies as [17]

$$S(q_z,q_\perp=0)\sim|q_z-2\pi m/d|^{\eta_m-2}\ . \tag{32}$$

The Caille exponent η_m of the mth-order Bragg peak is given by

$$\eta_m=m^2Tq_0^2/[8\pi(KB)^{1/2}]\sim m^2q_0\lambda/r\ . \tag{33}$$

The exponent η_m eventually becomes greater than 2 for m large enough, and the quasi-Bragg divergence becomes a cusp.

Observe that the coefficient of m^2 in the Caille exponent is precisely the inverse of the characteristic ratio in Eq. (31) describing unbinding of dislocations. Hence as $N\to\infty$, the Bragg peaks at progressively higher order survive undulation fluctuations. Again, the copolymer smectic phase becomes better ordered in the limit $N\to\infty$ even though the transition becomes second order in this limit.

VI. CONCLUSIONS

We have used two complementary methods to examine the possibility of nematic, rather than smectic, order in systems described by the Brazovskii model. We first constructed a generalization of Brazovskii's treatment of the IS transition in order to examine the stability of the isotropic phase to the formation of the nematic order. We find that, for anisotropic quartic interactions, the isotropic phase can become unstable to a nematic phase, but only at temperatures below the IS transition temperature. For strongly anisotropic interactions, however, both transition temperatures are of the same order in λ below the mean-field transition, necessitating a quantitative analysis. We then examined the stability of the low-temperature smectic phase with respect to dislocation-mediated melting into a nematic phase treating only the case of an isotropic interaction. We find that the stability of the smectic phase of diblock copolymers at temperatures just below the IS transition increases with N. More generally, we find that the smectic phase of the Brazovskii model is stable over the entire range of parameters in which Brazovskii's Hartree approximation is valid, and that it becomes increasingly stable as the transition becomes more weakly first order.

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