LANDAU–BRAZOVSKII THEORY FOR THE Ia3d STRUCTURE

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The stability of the so-called "Gyroid" phase, of $Ia3d$ symmetry, observed for lyotropic liquid crystals and block copolymers is accounted for using the Landau–Brazovskii theory of weak crystallization. In the mean field approximation, the $Ia3d$ phase is stable between the lamellar and hexagonal phases close to the disordered liquid phase. When allowance is made for Brazovskii critical fluctuations, a direct phase transition between the disordered liquid and $Ia3d$ phases is shown to be possible, in agreement with experimental observations.

Bicontinuous cubic phases are remarkable structures formed by certain amphiphiles [1,2], lipids [1,2] and block copolymers [3-5]. They are typically observed in a narrow phase diagram window between regions of stability of the lamellar (lam.) and hexagonal-packed cylinder (hex.) phases, close to the disordered liquid (isotropic) phase. The most commonly observed structure belongs to the $Ia3d$ space group, and the local morphology of this phase has been shown to be similar to the gyroid minimal surface [6].

The stability of an $Ia3d$ phase with respect to the lam. and hex. phases was first shown theoretically by Matsen and Schick, using numerical mean field theory calculations for diblock copolymers [7]. This structure was found to be stable between these 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 liquid phase to the $Ia3d$ phase observed experimentally [3,5] is not predicted.

In this letter, we investigate the stability of the $Ia3d$ phase using the Landau–Brazovskii (LB) theory of weak crystallization [8,9]. The approach is general for systems that undergo a weak phase transition driven by a short-wavelength instability between the disordered liquid and ordered crystalline phases. Thus it can be applied to thermotropic and lyotropic liquid crystals, as well as block copolymers [10,11]. The principal advantage of the LB theory compared to other theoretical methods is that it allows for thermal fluctuations of the short-wavelength component of the density function.

In the vicinity of a weak phase transition between the disordered liquid and an ordered crystalline phase, the density function of the system can be written as

$$\varrho(\mathbf{r}) = \varrho_0 + \delta\varrho(\mathbf{r}) \ , \tag{1}$$

where ϱ_0 is the uniform component insensitive to the phase transition, and $\delta\varrho(\mathbf{r})$ is the short-wavelength component characterizing crystalline order. The LB free energy functional describing this phase transition can be written in units of $k_B T$ as [12]

$$H[\delta\varrho] = \int dV \left[\frac{\tau}{2}\delta\varrho^2 + \frac{\xi_0^2}{8q_0^2}\left[(\nabla^2 + q_0^2)\delta\varrho\right]^2 - \frac{\gamma}{3!}\delta\varrho^3 + \frac{\lambda}{4!}\delta\varrho^4 \right] \ . \tag{2}$$

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Here τ is the reduced temperature, q_0 is the critical wavenumber, ξ_0 is the bare correlation length and γ, λ are phenomenological constants ($\lambda > 0$). For the system to be close to the short-wavelength instability it is assumed that

$$|\tau| \ll \xi_0^2 q_0^2. \tag{3}$$

The ordering transition (crystallization) 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. In the LB theory the condensate wavevectors lying on the sphere are chosen as the shortest reciprocal lattice vectors. Then the number and position of all condensate wavevectors may be determined using the expressions for allowed Bragg reflections [13]. Thus in the LB theory the set of the shortest reciprocal lattice vectors corresponds to the main harmonic of the density function, whereas the other reciprocal lattice vectors (lying off the sphere) correspond to the higher order harmonics.

In general, the short-wavelength component of the density function can be written as

$$\delta\varrho(\mathbf{r}) = \delta\varrho_{cr}(\mathbf{r}) + \eta(\mathbf{r}) \ , \tag{4}$$

where $\delta\varrho_{cr}(\mathbf{r})$ is the "crystalline" component possessing the symmetry of the crystal lattice, and $\eta(\mathbf{r})$ is the fluctuating component, with a thermodynamic average equal to zero. In turn, the "crystalline" component is [14]

$$\delta\varrho_{cr}(\mathbf{r}) = \sum_n \varrho_n \, \varphi_n(\mathbf{r}) \ , \tag{5}$$

where n is an index labelling harmonics, ϱ_n are the amplitudes playing the role of order parameters, and

$$\varphi_n(\mathbf{r}) = (2N_n)^{-1/2} \sum_{i=1}^{N_n} [e^{i(\mathbf{G}_{ni}\mathbf{r} + \alpha_{ni})} + \text{ c.c.}] \tag{6}$$

are orthonormal basis functions. The $\mathbf{G}_{ni}$ are the wavevectors of the reciprocal lattice forming the star of wavevectors of the nth harmonic ($|\mathbf{G}_{ni}| = G_n$), $2N_n$ is the number of arms in the star and the α_{ni} are fixed phases. In centrosymmetric structures, the phases α_{ni} are equal to 0 or π. The relative values of α_{ni} are fixed by the symmetry of the crystal lattice and can be determined using expressions for the geometrical structure factor tabulated in [13]. Unnormalized basis functions can be found in the same reference [7].

The basis functions can naturally be ordered using the parameter

$$\epsilon_n = \left(\frac{G_n^2}{q_0^2} - 1 \right)^2 \ , \tag{7}$$

starting from $\epsilon_1 = 0$, that corresponds to the main harmonic. The parameter ϵ_n naturally appears in the LB theory and characterizes the relative distance of wavevectors of the nth harmonic from the sphere $|q| = q_0$. Note that, in view of inequality (3), the sum in (5) is restricted to the set of harmonics with $\epsilon_n \ll 1$.

Within the classical LB theory, lam., hex. (two dimensional $P6m$), and b.c.c. ($Im3m$) structures compete for stability [15]. For these structures $\epsilon_2^{lam} = 9$, $\epsilon_2^{hex} = 4$, and $\epsilon_2^{Im3m} = 1$. Thus the analysis of the stability of the lam., hex., and $Im3m$ structures is performed in the one harmonic approximation. The basis functions corresponding to the main harmonic of these structures are [13,15]

$$\varphi_1^{lam}(x, y, z) = \sqrt{2} \cos q_0 z \ , \tag{8a}$$

$$\varphi_1^{hex}(x, y, z) = \sqrt{\frac{2}{3}} \left[\cos q_0 x + 2 \cos \frac{q_0 x}{2} \cos \frac{\sqrt{3} q_0 y}{2} \right] \ , \tag{8b}$$

$$\varphi_1^{Im3m}(x, y, z) = \sqrt{\frac{4}{3}} \left[\cos \frac{q_0 x}{\sqrt{2}} \cos \frac{q_0 y}{\sqrt{2}} + \cos \frac{q_0 y}{\sqrt{2}} \cos \frac{q_0 z}{\sqrt{2}} + \cos \frac{q_0 z}{\sqrt{2}} \cos \frac{q_0 x}{\sqrt{2}} \right] . \quad (8c)$$

In the mean field approximation the free energies for lam., hex. and $Im3m$ phases are then given by the equations [12,16]

$$F_{MF}^{lam} = \frac{\tau}{2} \varrho_1^2 + \frac{\lambda}{4!} \frac{3}{2} \varrho_1^4 , \quad (9a)$$

$$F_{MF}^{hex} = \frac{\tau}{2} \varrho_1^2 - \frac{\gamma}{3!} \sqrt{\frac{2}{3}} \varrho_1^3 + \frac{\lambda}{4!} \frac{5}{2} \varrho_1^4 , \quad (9b)$$

$$F_{MF}^{Im3m} = \frac{\tau}{2} \varrho_1^2 - \frac{\gamma}{3!} \sqrt{\frac{4}{3}} \varrho_1^3 + \frac{\lambda}{4!} \frac{15}{4} \varrho_1^4 . \quad (9c)$$

The mean field phase diagram for competing lam., hex. and $Im3m$ structures is well known [12]. Except for $\gamma = 0$, the $Im3m$ phase appears first upon crystallization due to the relatively large cubic coefficient [15]. 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 the LB theory does not take into account the fact that the wavevectors of the second harmonic [220] for the $Ia3d$ structure are uniquely close to the sphere $|q| = q_0$, occupied by the wavevectors of the main harmonic [211]. Indeed, for the $Ia3d$ structure $\epsilon_2^{Ia3d} = 1/9$, and this is at least an order of magnitude smaller than for other competing structures (it should also be noted that $\epsilon_3^{Ia3d} = 16/9$). Thus unlike the lam., hex. and $Im3m$ phases, the stability of the $Ia3d$ phase should be analysed in the two harmonic approximation. The basis functions corresponding to the first two harmonics of the $Ia3d$ structure are (cf.[17])

$$\varphi_1^{Ia3d}(x, y, z) = \sqrt{\frac{8}{3}} \left[\cos \frac{q_0 x}{\sqrt{6}} \sin \frac{q_0 y}{\sqrt{6}} \sin \frac{2q_0 z}{\sqrt{6}} + \cos \frac{q_0 y}{\sqrt{6}} \sin \frac{q_0 z}{\sqrt{6}} \sin \frac{2q_0 x}{\sqrt{6}} \right.$$
$$\left. + \cos \frac{q_0 z}{\sqrt{6}} \sin \frac{q_0 x}{\sqrt{6}} \sin \frac{2q_0 y}{\sqrt{6}} \right] , \quad (10a)$$

$$\varphi_2^{Ia3d}(x, y, z) = \sqrt{\frac{4}{3}} \left[\cos \frac{2q_0 x}{\sqrt{6}} \cos \frac{2q_0 y}{\sqrt{6}} + \cos \frac{2q_0 y}{\sqrt{6}} \cos \frac{2q_0 z}{\sqrt{6}} + \cos \frac{2q_0 z}{\sqrt{6}} \cos \frac{2q_0 x}{\sqrt{6}} \right] .$$
$$(10b)$$

The mean field free energy for the $Ia3d$ phase is given by the equation

$$F_{MF}^{Ia3d} = \frac{\tau}{2} \varrho_1^2 - \frac{\gamma}{3!} \frac{1}{\sqrt{6}} \varrho_1^3 + \frac{\lambda}{4!} \frac{17}{8} \varrho_1^4 + \frac{1}{2} (\tau + \frac{1}{4} \epsilon_2^{Ia3d} \xi_0^2 q_0^2) \varrho_2^2 - \frac{\gamma}{3!} \frac{2}{\sqrt{3}} \varrho_2^3 + \frac{\lambda}{4!} \frac{15}{4} \varrho_2^4$$
$$+ \frac{\gamma}{3!} \frac{\sqrt{3}}{2} \varrho_1^2 \varrho_2 + \frac{\lambda}{4!} 3 \varrho_1^2 \varrho_2^2 . \quad (11)$$

A comparative analysis of the free energy of the different phases shows that allowance for the second harmonic [220] of the $Ia3d$ phase in addition to the principal one [211], results in stabilisation of the latter 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 (fig.1). The triple point is located at $|\tau| \sim \epsilon_2^{Ia3d} \xi_0^2 q_0^2$, where the second harmonic [220] of the $Ia3d$ phase becomes important for the first time. This result is in qualitative agreement with [7], where numerical mean field calculations for diblock copolymers were performed.
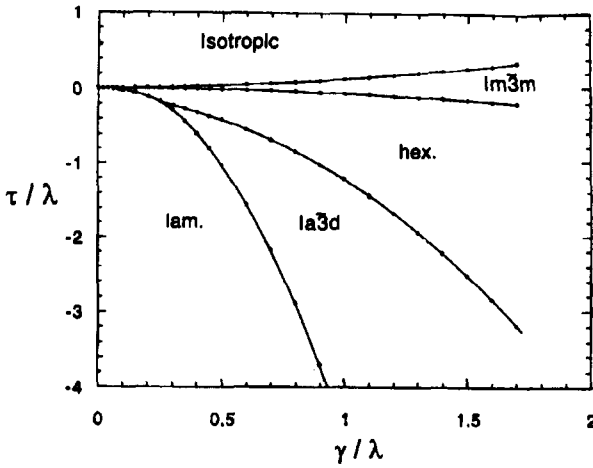
Fig.1. Mean field phase diagram for isotropic, lam., hex., $Im3m$ and $Ia3d$ phases, for the case $\xi_0^2 q_0^2 / 4\lambda = 1$. Transitions were located numerically at the positions located with filled circles, the lines are drawn as guides to the eye

In the presence of thermal fluctuations the total free energy of the system is given by

$$F = F_{MF} - \ln \int e^{-\tilde{H}[\eta]} \mathcal{D}\eta \ . \tag{12}$$

Here

$$\tilde{H}[\eta] = \int dV \left[\frac{\tau}{2}\eta^2 + \frac{\xi_0^2}{8q_0^2}\left[(\nabla^2 + q_0^2)\eta\right]^2 - \frac{\gamma}{3!}\eta^3 + \frac{\lambda}{4!}\eta^4 + \frac{\xi_0^2}{4q_0^2}\left[(\nabla^2 + q_0^2)^2\delta\varrho_{cr}\right]\eta \right.$$

$$\left. - \frac{\gamma}{2!}\delta\varrho_{cr}\eta^2 - \frac{\gamma}{2!}\delta\varrho_{cr}^2\eta + \frac{\lambda}{3!}\delta\varrho_{cr}\eta^3 + \frac{\lambda}{3!}\delta\varrho_{cr}^3\eta + \frac{\lambda}{4}\delta\varrho_{cr}^2\eta^2 \right] \tag{13}$$

is an exact free energy functional for fluctuations.

As shown by Brazovskii [9], when the inequality (3) is fulfilled, the effect of thermal fluctuations may be considered in a lower non-trivial (Hartree) order of self-consistent perturbation theory (SCPT). Recall that in SCPT, the exact functional $\tilde{H}$ is replaced by some effective Gaussian functional $\tilde{H}_{eff}^{(0)}$, and the difference $\tilde{H} - \tilde{H}_{eff}^{(0)}$ is considered as a small perturbation. The series of terms in SCPT appear in the same form as in thermodynamic perturbation theory [14]. The only difference is that the parameters of the functional $\tilde{H}_{eff}^{(0)}$ are determined self-consistently from the condition of the minimum of the appropriate approximate free energy.

In the Hartree order of SCPT, the "bare" approximate free energy has the form (cf.[14]):

$$F_{appr} = F_{MF} - \ln \int e^{-\tilde{H}_{eff}^{(0)}} \mathcal{D}\eta + \left\langle \tilde{H} - \tilde{H}_{eff}^{(0)} \right\rangle_0 \ , \tag{14}$$

where $\langle ... \rangle_0$ denotes the thermodynamic average calculated using the effective functional $\tilde{H}_{eff}^{(0)}$. In turn, the effective Gaussian functional is

$$\tilde{H}_{eff}^{(0)}[\eta] = \frac{1}{2}\int dV \left[r\eta^2 + \frac{\xi_0^2}{4q_0^2}\left[(\nabla^2 + q_0^2)\eta\right]^2 \right] \ , \tag{15}$$

where the gap r is determined from the condition that the first variational derivative of the approximate free energy (14) with respect to r vanishes.

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It can be shown that for lam., hex. and $Im3m$ phases [9]

$$r = \tau + \frac{\lambda}{2}\langle \eta^2 \rangle_0 + \frac{\lambda}{2}\varrho_1^2 \ , \tag{16a}$$

whereas for the $Ia3d$ phase

$$r = \tau + \frac{\lambda}{2}\langle \eta^2 \rangle_0 + \frac{\lambda}{2}(\varrho_1^2 + \varrho_2^2) \ . \tag{16b}$$

Here, the self-consistent value of the mean-square fluctuation $\langle \eta^2 \rangle_0$ is

$$\langle \eta^2 \rangle_0 = \frac{2\alpha}{\sqrt{r}} \ , \tag{17}$$

where $\alpha = \dfrac{q_0^2}{4\pi \xi_0}$ [9].

The Hartree free energy (the optimal value of the approximate free energy (14)) is then given by

$$F_{Hartree} = F_{MF} - \ln \int e^{-\tilde{H}_{eff}^{(0)}} \mathcal{D}\eta - \frac{\lambda}{8}\langle \eta^2 \rangle_0^2 \ . \tag{18}$$

The first term in (18) is the condensate free energy, the second is the free energy of an effective Gaussian field, and the last is the so-called "correlation" free energy.

Using eq.(17) and performing Gaussian functional integration in (18), the final expression for the Hartree free energy takes the following simple form:

$$F_{Hartree} = F_{MF} + 2\alpha\sqrt{r} - \frac{\lambda}{2}\frac{\alpha^2}{r} \ . \tag{19}$$

Note that this expression gives the *absolute* value of the Hartree free energy in the LB theory, whereas the well-known equation of Brazovskii (eq.(13b) in ref.[9]) gives the *difference* between the Hartree free energies of the disordered liquid and crystalline phases.

The principal requirement for validity of the LB theory when allowance for critical fluctuations is made is that the value of $|\tau|$ at Brazovskii transition (transition from the disordered liquid to the lamellar phase), $|\tau_{Br}| \sim (\alpha\lambda)^{2/3}$ [9], satisfies the inequality (3), or

$$\kappa \equiv \frac{(\alpha\lambda)^{2/3}}{\xi_0^2 q_0^2} \ll 1 \ . \tag{20}$$

We assume here that the value of r at the Brazovskii transition (r_{Br}) is of the order of $|\tau_{Br}|$, so the inequality (20) guarantees satisfaction of the Brazovskii criterion $r_{Br} \gg \alpha\lambda(\xi_0 q_0)^{-1}$ [9]. This ensures the smallness of higher order corrections to the Hartree free energy up to the phase transition line. Attempts to confirm via numerical calculations that at the Brazovskii transition $r_{Br} \ll |\tau_{Br}|$ are unfounded, because in Brazovskii theory there exists no small parameter, apart from $|\tau_{Br}|$, that controls the relative value of r_{Br}. It therefore appears that the estimate of the lower bound of validity of the Brazovskii theory for the case of block copolymers $(N \geq 10^{10}$, where N is the degree of polymerization) used by Fredrickson and Helfand [10] is incorrect.

The allowance for critical Brazovskii fluctuations results, as usual, in an expansion of the stability region of the disordered liquid phase to lower temperatures [9]. In fig.2 we present phase diagrams calculated using eq.(19) in terms of $\tilde{\tau} = \tau(\alpha\lambda)^{-2/3}$ and $\tilde{\gamma} = \gamma(\alpha\lambda)^{-1/3}\lambda^{-1/2}$. For $0 < \kappa < \kappa^*$ $(\kappa^* = 0.06)$ the order-disorder transition line is closer to the stability region of the $Ia3d$ phase than in the mean field approximation. As the value of κ increases, the order-disorder line approaches the triple point, this corresponds to the increasing importance of

fluctuations. Finally, at $\kappa \geq \kappa^*$ there is a direct transition between the disordered liquid and the $Ia3d$ phases. The threshold value $\kappa^* \sim \epsilon_2^{Ia3d}$ corresponds to the situation when the Brazovskii transition takes place at $|\tau_{Br}| \sim \epsilon_2^{Ia3d}\zeta_0^2 q_0^2$, where the second harmonic of the $Ia3d$ phase becomes important for the first time.
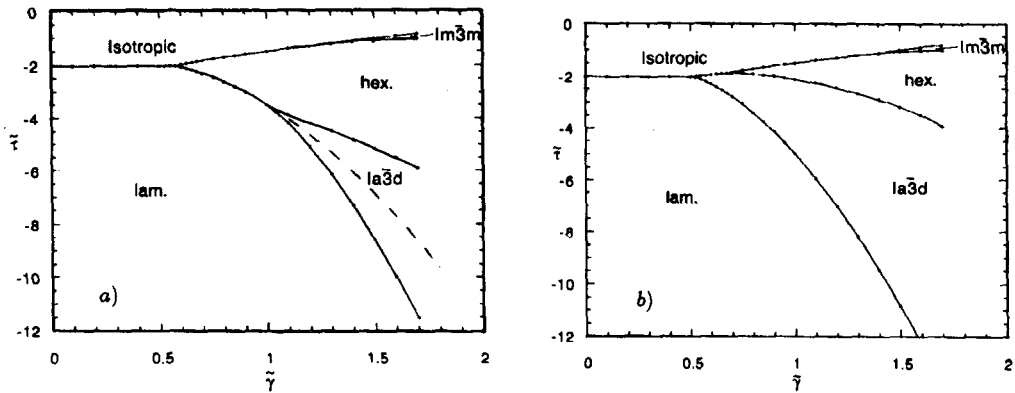

Fig.2. Phase diagrams calculated allowing for Brazovskii critical fluctuations, using eq.(19). Phase diagrams are presented with κ equal to (a) 0.015, (b) 0.15. The dashed line shows the lam.-hex. virtual phase transition line

Thus we have shown that the second harmonic [220] in addition to the principal one [211] is responsible for the stability of the $Ia3d$ phase with respect to the lam. and hex. phases just below the order-disorder transition line. In turn, fluctuations are responsible for shifting the order-disorder line to lower temperatures, and as a result, for direct phase transitions between the disordered liquid and the $Ia3d$ phases. These results are in qualitative agreement with experimental observations on lyotropic liquid crystals, and especially, weakly segregated diblock copolymers.

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