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Landau theory for smectic-*A*–hexatic-*B* coexistence in smectic films

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We explain theoretical peculiarities of the smectic-*A*–hexatic-*B* equilibrium phase coexistence in a finite-temperature range recently observed experimentally in free-standing smectic films [I. A. Zaluzhnyy *et al.*, Phys. Rev. E **98**, 052703 (2018)]. We quantitatively describe this unexpected phenomenon within Landau phase transitions theory assuming that the film state is close to a tricritical point. We found that the surface hexatic order diminishes the phase coexistence range as the film thickness decreases, shrinking it to zero at some minimal film thickness L_c, of the order of a few hexatic correlation length. We established universal laws for the temperature width of the phase coexistence range in terms of the reduced variables. Our theory is in agreement with the existing experimental data.

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I. INTRODUCTION

Free-standing smectic films are unique layered systems, solidlike in one direction (normal to the layers) and fluidlike in two lateral directions. Unlike other films, smectic films are living in the three-dimensional (3D) world without any parasitic influence from a substrate. It is not surprising that this topic is the subject of many experimental and theoretical works (see, e.g., the comprehensive review [1] and the monograph [2]). Our motivation to add one more article to the investigation field is related to new results concerning the phase coexistence in smectic films that we obtained. Our main concern is related to finite-size effects.

In our study we develop the quantitative theory explaining the finite-temperature interval for the equilibrium coexistence of the smectic-*A* (Sm-*A*) and the hexatic *B* (Hex-*B*) phases in the smectic films.

Common wisdom claims that the equilibrium phase coexistence at the first-order phase transition in the unconfined one-component material takes place at the transition temperature solely. Indeed, only at the transition point do both coexistent phases have equal free energies (cf., with the phase coexistence between spinodal and binodal lines, when one of the coexisting phase is in a metastable state). A finite range for the phase coexistence can be achieved for binary mixtures, or (in the case of a pure one-component material) in confined geometry, where neither of the coexistent states can provide the required equilibrium density. However, in our case the Sm-*A*-Hex-*B* phase transition occurs in one-component material and in apparently unconfined free-standing film geometry. The point is that any smectic liquid crystal is a strongly anisotropic system (solidlike along the normal to smectic layers). Due to this anisotropy, smectic stress tensor components orthogonal to the smectic layers are not determined uniquely by the external pressure, as an essential contribution comes from the solidlike elasticity of smectic layers (see more details in Refs. [1,2]). As a result, smectic films behave similarly to a closed volume (i.e., confined) system undergoing a first-order phase transition under conditions where the number of the smectic layers is fixed (i.e., unchanged on a timescale needed to get the equilibrium phase coexistence). The standard experimental technique for the free-standing smectic film preparation provides the uniform film thickness [3–7]. In turn, local changes in the film thickness are possible only under overheating of the free-standing smectic film above the bulk temperature of melting of the smectic phase or under local (nonuniform) heating of the films, see Refs. [4–13]. These nonequilibrium phenomena are beyond our consideration.

Being motivated by the experiment in Ref. [3] we consider only relatively thick films, i.e., three-dimensional systems. Similarly to the Sm-*A*–Sm-*C* phase transition the Sm-*A*–Hex-*B* phase transition means a reduction of the rotational symmetry of the smectic layers. In the Sm-*A* state the layers are isotropic, whereas in the hexatic smectics the layers possess a sixth-order rotational axis. The corresponding order parameter is a six-order symmetric irreducible tensor Q_{injklm} (its irreducibility means $Q_{iijklm} = 0$), having the components only along the layers. The tensor Q_{injklm} has two independent components [14,15], a linear combination of which is the scalar complex field ψ. Its phase is changed by the angle 6φ at the rotation of the reference frame by the angle φ. Due to the rotational invariance of the Sm-*A* phase, the Landau functional has to be invariant under a phase shift of ψ. Therefore one would expect a second-order phase transition with the *XY* universality class. However, in a majority of the materials, exhibiting Sm-*A*-Hex-*B* phase transition, it is of weak first order, see Refs. [1,3,8,16–20].

A tempting explanation of the fact assuming that the transition is close to a critical point is excluded since the states have different symmetries (Sm-*A* possesses isotropic

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liquidlike smectic layers, and Hex-*B* possesses orientation hexagonal symmetry order). We suggest another possibility to explain the experimental data when the system is close to a tricritical point. This assumption is supported also by the measured critical exponents (for the specific heat and for the order parameter) that are close to those for the tricritical point [16–18,21]. It is worth noting that the liquid-crystalline materials exhibiting the Sm-*A*-Hex-*B* phase transition demonstrate apparently universal behavior. The phase diagrams of such materials are remarkably similar even though the molecules of the materials are appreciably different (see, for example, Refs. [19,20]). Thus our results are universal and can be applied to all such materials.

We exploit the phenomenological Landau phase transitions theory. As it is known, the mean-field Landau theory works well near the tricritical point (up to logarithmic corrections), see, e.g., Refs. [22–24]. Our calculations are mainly analytical, giving the framework for observable effects. They are expressed as universal laws in terms of reduced variables. To find solutions of the nonlinear equations within the whole temperature interval of the phase coexistence we use Wolfram Mathematica numerics. This allows us to illustrate dependencies for the width of the equilibrium phase coexistence on system parameters. We also compute numeric values of the dimensionless coefficients entering the derived analytically universal laws.

In Ref. [3] the coexistence of Sm-*A* and Hex-*B* phases was observed in a finite-temperature interval (and qualitatively and semiquantitatively, for thick films, rationalized theoretically). However, in Ref. [3] the expression for the temperature interval of the equilibrium phase coexistence has been derived merely from the surface order-induced renormalization of the bulk hexatic phase parameters (what is not a consistent procedure). In this work we present the consistent quantitative theory.

Our paper is organized as follows. In Sec. II we formulate general thermodynamical conditions for the phase coexistence in a form suitable for smectic liquid crystals possessing the layer structure. In Sec. II A we discuss the phase coexistence in bulk in terms of the Landau theory. Specifically motivated by experimental observations [3] we study the Sm-*A*-Hex-*B* transition in the free-standing films. In Sec. III we explore and analyze the key point of our work, namely the surface effects. In the free-standing smectic films exhibiting the Sm-*A*-Hex-*B* phase transition, the surface hexatic order occurs at the temperature higher than the bulk transition temperature. The surface-induced order in the vicinity of a tricritical point penetrates into the interior of the film, which essentially influences the phase transition even for relatively thick films, which are the systems of our special interest. This phenomenon is the subject of our consideration in this work. In particular, we demonstrate that the surface order provokes diminishing of the phase coexistence range as the film thickness decreases. Eventually, it leads to shrinkage of the coexistence range at some minimal film thickness L_c. Thus we arrive at a special critical point, where the coexisting phases become indistinguishable. In Sec. IV, we summarize our results and also discuss some open questions and perspectives. We relegate some technical details of the analytic calculations into two Appendices to the main text.

II. GENERAL THERMODYNAMIC ANALYSIS OF THE PHASE COEXISTENCE

Here we present the general thermodynamical conditions of the phase coexistence [22,25]. Two-phase coexistence indicates that none of the coexisting phases (in our case Sm-*A* and Hex-*B*) is able to support the optimal two-dimensional density of the film, and the compromise is achieved by means of two-phase equilibrium where two phases coexist. The coexistence signals about first-order transition between the phases. However, ordering in the hexatic case is weak in the region of the phase coexistence. That enables one to use the Landau expansion in the order parameter to analyze the phenomenon. We consider the case where the number of the smectic layers in the film is fixed. The assumption holds if nucleation of dislocation loops (which are able to adjust the number of layers to the external stresses) is very infrequent and too slow in comparison to characteristic time scales relevant for the phase coexistence [2,26,27]. Then the thickness L of the film is determined as a minimum condition of an appropriate thermodynamic potential. The thicknesses of the Sm-*A* and Hex-*B* phases are slightly different (at a given temperature); however, due to the weakness of the hexatic ordering the difference is small and can be safely neglected.

We designate as N_H and N_A two-dimensional mass densities and designate as F_H and F_A two-dimensional free-energy densities of the Hex-*B* and Sm-*A* phases, respectively. The areas the phases occupy are A_H and A_A, and then the total free energy of the system can be written as

$$\begin{aligned}\mathcal{F} = F_A(N_A)A_A + F_H(N_H)A_H \\ - \mu(N_A A_A + N_H A_H - \mathcal{N}),\end{aligned} \tag{1}$$

where $\mathcal{N}$ is the total number of molecules in the film and μ is a Lagrangian multiplier fixing the number. Minimization of the energy (1) in terms of N_A and N_H leads to the conditions

$$\frac{\partial F_A}{\partial N_A} = \mu = \frac{\partial F_H}{\partial N_H}. \tag{2}$$

Thus the chemical potentials of the phases are equal if they coexist. This condition is analogous to famous Maxwell common tangent construction, see Refs. [23–25,28].

Note that $A_H = A - A_A$, where A is the total area of the film. Therefore minimization of the expression (1) in terms of A_A leads to the condition

$$\Omega_A = \Omega_H, \tag{3}$$

where Ω is the grand thermodynamic potential per unit area:

$$\begin{aligned}\Omega(\mu) = F - N\frac{\partial F}{\partial N}, \quad \mu = \frac{\partial F}{\partial N}, \\ d\Omega = -N d\mu - S dT.\end{aligned} \tag{4}$$

Further, we operate in terms of the grand thermodynamic potential having in mind that both the chemical potentials and the temperatures of the coexisting phases should coincide.

We arrived at the following general picture of the phase transition. At $T > T_+$ the Sm-*A* phase is realized. Then the chemical potential μ is determined by the condition $\partial\Omega_A/\partial\mu = -N$, where $N = \mathcal{N}/A$ is the average two-dimensional density of molecules of the film. At $T < T_-$ the

Hex-*B* phase is realized. Then the chemical potential μ is determined by the condition $\partial\Omega_H/\partial\mu = -N$. At $T_- < T < T_+$ the phases coexist, and then the chemical potential μ is determined by the condition (3). Thus, the chemical potential μ_+ at $T = T_+$ is determined by the relation (3) and the condition $\partial\Omega_A/\partial\mu = -N$.

Below T_+, in the region of the phase coexistence, the density of the Sm-*A* phase $N_A = -\partial\Omega_A/\partial\mu$ does not coincide with N. We expect that it is larger than N: $N_H < N < N_A$. Having in mind narrowness of the coexistence region, we expand the density of the Sm-*A* phase in $\mu - \mu_+$, $T - T_+$ to obtain

$$N_A = N - \frac{\partial^2\Omega_A}{\partial\mu^2}(\mu - \mu_+) - \frac{\partial^2\Omega_A}{\partial T\partial\mu}(T - T_+), \tag{5}$$

where the derivatives are taken at $T = T_+$, $\mu = \mu_+$.

A. Landau expansion

The hexatic order parameter ψ (see its definition above and more details can be found in Refs. [14,28,29]) in the region of the phase coexistence is assumed to be small. Then one may expand the grand thermodynamic potential Ω in ψ to obtain $\Omega = \Omega_0 + \Phi$, where Φ is the Landau functional. In the context of the bulk consideration (neglecting surface effects) the first terms of its expansion in ψ are

$$\Phi = L(a|\psi|^2 - \lambda|\psi|^4/6 + \zeta|\psi|^6/90), \tag{6}$$

where L is the thickness of the film and the coefficients a, λ, and ζ are functions of T and μ.

We expanded the grand thermodynamic potential Ω up to the sixth order in ψ having in mind that both coefficients, a and λ, are anomalously small. In other words, the system is in the tricritical regime (near a tricritical point in the phase diagram). It is well known [22–24] that in the tricritical regime fluctuations of the order parameter are relatively weak: They produce only logarithmic corrections to observable quantities. Therefore our problem can be examined in the mean-field approximation.

To find equilibrium values of the order parameter ψ, one should minimize the Landau functional (6). The Sm-*A* phase corresponds to the zero value of the order parameter ψ. The minimum of Φ at $\psi = 0$ is realized if $a > 0$, and the condition is implied below. The Hex-*B* phase corresponds to a non-zero-order parameter that can be found as a result of the following minimization:

$$|\psi_m|^2 = \frac{5\lambda}{\zeta}\left(1 + \sqrt{1 - \frac{6a\zeta}{5\lambda^2}}\right). \tag{7}$$

This minimum of the Landau functional exists if $6a\zeta < 5\lambda^2$.

In the mean-field approximation the Landau functional Φ is equal to zero for the Sm-*A* phase. Therefore $\Omega_A = \Omega_0$, $\Omega_H = \Omega_0 + \Phi_H$. Since $\Omega_H = \Omega_A + \Phi_H$, we obtain

$$N_H = N_A - \partial\Phi_H/\partial\mu \tag{8}$$

in the region of the phase coexistence. Note that at calculating the derivative in Eq. (8) one can differentiate only the coefficients in the expansion (6) since $\partial\Phi/\partial\psi = 0$ in the minimum.

To find the value of the order parameter in the regime of phase coexistence one should use the relation (3). In our case it leads to $\Phi_H = 0$. Substituting the expression (7) into Eq. (6) and equating the result to zero, one finds $a = a_0$, $|\psi| = \psi_0$, where the equilibrium value of the order parameter is

$$\psi_0^2 = 15\lambda/(2\zeta), \quad a_0 = (5/8)\lambda^2/\zeta. \tag{9}$$

Thus, both parameters ψ and a are fixed by the equilibrium conditions. Note the relation $\zeta a \sim \lambda^2$ between two small parameters, a and λ.

Within Landau theory, the parameter a in the expansion (6) is the most sensitive to variations of chemical potential μ and of temperature T. Therefore in the main approximation we can safely assume that the coefficients λ and ζ are independent of the temperature and of the chemical potential in the phase coexistence region. In the same spirit we believe that the equilibrium phase coexistence exists in the narrow range of the parameters governing the transition. As we will show below it is the case in the vicinity of the tricritical point. Thus we expand a in $T - T_+$ and $\mu - \mu_+$ to obtain

$$a = a_+ + \alpha(T - T_+) + \beta(\mu - \mu_+), \tag{10}$$

where a_+ is the value of the parameter a at $T = T_+$ and $\mu = \mu_+$. We expect that both coefficients, α and β, are positive. The conditions mean that on diminishing T or μ the hexatic phase becomes more preferable.

In our model the only quantity in the Landau functional (6), dependent on μ, is a. Calculating $\partial\Phi/\partial\mu$, and substituting then the value (9), we find in accordance with Eq. (8)

$$N_H = N_A - L\beta\frac{15\lambda}{2\zeta}. \tag{11}$$

As we expected, there is an additional negative contribution to N_H in comparison with N_A. In our model, it is independent of T.

The condition $a = a_0$ shows that at the phase coexistence a remains approximately constant, that is. $\alpha(T - T_+) + \beta(\mu - \mu_+) = 0$. Substituting the relation into the expression (5) and the resulting formula for N_A into expression (11), we obtain

$$N_H = N - L\beta\frac{15\lambda}{2\zeta} + \Gamma L(T_+ - T), \tag{12}$$

$$\Gamma L = \frac{\partial^2\Omega_0}{\partial T\partial\mu} - \frac{\alpha}{\beta}\frac{\partial^2\Omega_0}{\partial\mu^2}. \tag{13}$$

The lower coexistence temperature T_- is achieved where N_H becomes N, and the property enables us to obtain the temperature interval of the phase coexistence in the bulk:

$$\frac{\Gamma}{\beta}(T_+ - T_-) = \psi_0^2 = \frac{15\lambda}{2\zeta}. \tag{14}$$

Since the phase transition occurs in the vicinity of the tricritical point, the coefficient λ is small. Therefore the interval $T_+ - T_-$ is small as well, as we have assumed expanding the coefficient a in (10), and $a_+ = a_- = a_0$ in the first order of the expansion of a over deviations $(T - T_+)$, $(\mu - \mu_+)$.

III. SURFACE EFFECTS

Here we consider effects related to the surface hexatic order (see Refs. [2,30–32], which contain many useful references). We assume that at the surface of the film the absolute value ψ_s of the hexatic order parameter ψ is fixed. Then the order parameter is nonzero and inhomogeneous in space in both phases. In the spirit of the mean-field treatment we assume that ψ is homogeneous along the film. However, due to the prescribed value of the surface ordering, it is inhomogeneous in the orthogonal direction. To analyze the situation one should introduce the Landau functional for the inhomogeneous order parameter. For this purpose we add the gradient term to the Landau expansion (6) and obtain

$$\Phi = \int_{-L/2}^{L/2} dz \left(b|\partial_z \psi|^2 + a|\psi|^2 - \frac{\lambda|\psi|^4}{6} + \frac{\zeta|\psi|^6}{90} \right), \tag{15}$$

where b is Landau theory expansion coefficient and the z axis is along the smectic layer normal.

To avoid confusion, it is worthwhile to stress that our phenomenological theory [with the squared gradient term in (15)] holds for relatively thick films (thus three-dimensional systems). Even for the minimal thickness film, when the phase coexistence region width shrinks to zero (see below) the film thickness is still larger than about five correlation lengths (along the normal to the smectic layers). Moreover, in the vicinity of the tricritical point the correlation length is much larger than the layer thickness. In such conditions the disclination-induced two-dimensional (Berezinskii-Kosterlitz-Thouless, see Refs. [33–38]) mechanism for the phase transition does not work because the energy of the disclination is much larger than the thermal energy.

We place the plane $z = 0$ in the center of the film. Let us stress that the surface ordering provides a nonzero value of the Landau functional for the Sm-A phase, in contrast to the analysis of the Sec. II, performed neglecting the surface effects. Since the gradient term is positive, the homogeneous configuration is a trivial minimizer of the Landau thermodynamic potential. In the bulk system, if the thermodynamic potential is convex, then a single homogeneous phase is a solution corresponding to a stable thermodynamic state. However, if, on the other hand, it is concave for some values of the model parameters, then it is energetically favorable to split the system into (at least) two regions with the phase coexistence. Conventional wisdom suggests that surface ordering plays a small role for bulk transitions for sufficiently thick films. Conventional wisdom is simple and comfortable but not necessarily always true. We will show in this section that it is just the case for the Sm-A-Hex-B transition in the vicinity of the tricritical point.

The characteristic length of the order parameter variations along the z axis is its correlation length ξ, defined as

$$\xi^2 = \frac{b}{a_0} = \frac{8b\zeta}{5\lambda^2}. \tag{16}$$

The quantity ξ is assumed to be much larger than the molecular length, and the property holds because the system is assumed to be close to a tricritical point. That justifies our phenomenological approach. Note also that in our approach the correlation length ξ weakly depends on temperature in the coexistence region.

Further on we assume that the order parameter ψ is real. The case corresponds to the minimum contribution from the gradient term in the Landau expansion (15). The constant (zero) phase does not enter into our mean-field analysis. Based on the up-down symmetry of the system we consider the symmetric in z profile of the order parameter: ψ is equal to ψ_s at $z = \pm L/2$ and achieves a minimum at $z = 0$.

Variation of the Landau functional (15) over ψ yields to the extremum condition

$$-b\partial_z^2\psi + a\psi - \lambda\psi^3/3 + \zeta\psi^5/30 = 0. \tag{17}$$

Equation (17) has the first integral:

$$-(\partial_z\psi)^2 + g(\psi) = \gamma, \tag{18}$$

$$g(\psi) = \frac{1}{b}(a\psi^2 - \lambda\psi^4/6 + \zeta\psi^6/90), \tag{19}$$

where γ is a z-independent parameter. As follows from Eq. (18), γ is the value of g at $z = 0$ where $\partial_z\psi = 0$ (since ψ is symmetric in z).

With the relation (18) taken into account, the energy (15) becomes

$$\Phi = 2b\int_0^{L/2} dz\,(2g - \gamma). \tag{20}$$

Equation (18) at $z > 0$ is rewritten as $\partial_z\psi = \sqrt{g - \gamma}$, that is, $dz = d\psi/\sqrt{g - \gamma}$. Integrating the condition, we find

$$L = 2\int_{\psi_\star}^{\psi_s} \frac{d\psi}{\sqrt{g - \gamma}}, \tag{21}$$

where $\psi_\star$ is the value of the order parameter at $z = 0$, $\gamma = g(\psi_\star)$ in accordance with Eq. (18) and ψ_s is the surface value of the order parameter.

Analogously, the Landau functional (20) can be rewritten as

$$\Phi = 2b\left[2\int_{\psi_\star}^{\psi_s} d\psi\,\sqrt{g - \gamma} + \gamma L/2\right]. \tag{22}$$

The expression determines the smectic energy per unit area of the phase with the surface conditions taken into account. The relation (21) can be treated as the extremum condition in terms of $\psi_\star$ (or γ) of the Landau functional (22).

In the vicinity of the tricritical point, ψ_s, entering into Eqs. (21) and (22), is much larger than the characteristic values of the order parameter ψ in the bulk. Therefore one can put $\psi_s \to \infty$ in Eq. (21) due to convergence of the integral. Thus we arrive at the function

$$\Xi(a, \gamma) = 2\int_{\psi_\star}^{\infty} \frac{d\psi}{\sqrt{g - \gamma}}, \tag{23}$$

to be equated to L in the equilibrium in accordance with Eq. (21).

A. Phase coexistence

In the phase coexistence region there are two different solutions of Eq. (18) satisfying the conditions (21) and corresponding to the same energies, $\Phi_A = \Phi_H$. We designate as ψ_A, ψ_H the values of the order parameter at $z = 0$ in the Sm-A phase and in the Hex-B phase, respectively. Introducing also $\gamma_A = g(\psi_A)$ and $\gamma_H = g(\psi_H)$, we arrive at the relations

$$\Xi(a, \gamma_A) = L = \Xi(a, \gamma_H). \tag{24}$$

The relations (24) together with the condition $\Phi_A = \Phi_H$ are three equations for the three variables L, γ_A, and γ_H.

Now we are in the position to find the difference $\Delta\Phi = \Phi_A - \Phi_H$:

$$\frac{\Delta\Phi}{b} = (\gamma_A - \gamma_H)L + 4\int_{\psi_A}^{\psi_H} d\psi\sqrt{g-\gamma_A} + 4\int_{\psi_H}^{\infty} d\psi(\sqrt{g-\gamma_A} - \sqrt{g-\gamma_H}), \tag{25}$$

in accordance with Eq. (22). Again, we extended the integration up to infinity due to convergence of the integral. One can easily check that

$$\frac{\Delta\Phi}{b} = \int_{\gamma_A}^{\gamma_H} d\gamma(\Xi - L). \tag{26}$$

Note that Eqs. (24) are extrema conditions for the quantity (26) in terms of γ_A and γ_H.

The difference $\Delta\Phi$ can be considered as a function of L, with the relation $b^{-1}\partial(\Delta\Phi)/\partial L = \gamma_A - \gamma_H < 0$. In addition, $\Delta\Phi$ is a function of a via the function g, see Eq. (19). Then the equilibrium condition $\Delta\Phi = 0$ determines L as a function of a. Therefore we obtain

$$\frac{\partial\Delta\Phi}{\partial a} + b(\gamma_A - \gamma_H)\frac{dL}{da} = 0. \tag{27}$$

Since the relations (24) are extrema conditions of $\Delta\Phi$ in terms of ψ_A, ψ_H, we find

$$\frac{\partial\Delta\Phi}{\partial a} = 2\int_{\psi_A}^{\psi_H} d\psi\,\psi^2/\sqrt{g-\gamma_A} + 2\int_{\psi_H}^{\infty} d\psi\,\psi^2(1/\sqrt{g-\gamma_A} - 1/\sqrt{g-\gamma_H}). \tag{28}$$

To find the value of L at a given a, one should solve the system of Eqs. (24) together with the condition $\Delta\Phi = 0$. The relations are reduced to the following system of equations:

$$\Xi(\gamma_A, a) = \Xi(\gamma_H, a), \tag{29}$$

$$\int_{\psi_A}^{\psi_H} d\psi\,(2g-\gamma_A)/\sqrt{g-\gamma_A} + \int_{\psi_H}^{\infty} d\psi\left(\frac{2g-\gamma_A}{\sqrt{g-\gamma_A}} - \frac{2g-\gamma_H}{\sqrt{g-\gamma_H}}\right) = 0, \tag{30}$$

determining ψ_A, ψ_H (see Fig. 1) and in turn γ_A, γ_H (see Fig. 2). The function Ξ in Eq. (29) is defined by Eq. (23).

After solving the system of Eqs. (29) and (30), L can be found from any of the relations (24). In other words, L is determined by the relation $L = \Xi(a, \gamma_A)$. The results of the numeric computations are shown in Figs. 3 and 4. Numeric solutions of Eqs. (29), (30), and (33) were obtained by the Wolfram Mathematica Professional Version Premier Service L3159-1472. The numeric errors of all our results are less than 5×10^{-6}.

B. Model Landau functional

Here we exploit the model, introduced above, where the parameter a is determined by the expansion (10) and the parameters λ and ζ are treated as constants, independent of temperature and chemical potential. In addition, we assume that the parameter b is constant as well. Then one finds from Eqs. (15), (18), and (22)

$$N_A = -\frac{\partial\Omega_A}{\partial\mu} = -\frac{\partial\Omega_0}{\partial\mu} - 2\beta\int_{\psi_A}^{\psi_s}\frac{d\psi\;\psi^2}{\sqrt{g-\gamma_A}} \tag{31}$$

and an analogous expression for the hexatic phase.

Since $N_A = N$ at $T = T_+$ and $N_H = N$ at $T = T_-$, the interval of the phase coexistence is determined by the condition $N_H(T_-) = N_A(T_+)$. According to Eq. (31), it is written as

$$\frac{\partial\Omega_0}{\partial\mu}(T_-,\mu_-) - \frac{\partial\Omega_0}{\partial\mu}(T_+,\mu_+) = 2\beta\int_{\psi_A}^{\psi_H}\frac{d\psi\;\psi^2}{\sqrt{g_+-\gamma_A}} + 2\beta\int_{\psi_H}^{\infty} d\psi\;\psi^2 \times\left(\frac{1}{\sqrt{g_+-\gamma_A}} - \frac{1}{\sqrt{g_--\gamma_H}}\right), \tag{32}$$

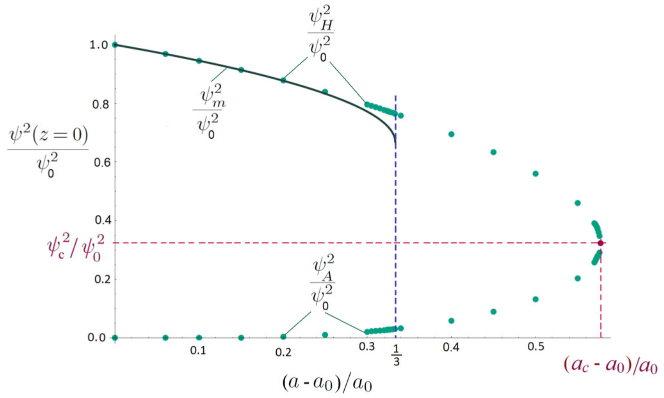

FIG. 1. Found numerically by solving Eqs. (29) and (30) values of the dimensionless value of the hexatic order parameter ψ^2/ψ_0^2 at $z = 0$ in the coexistence regime (sea-green circles) as a function of the dimensionless temperature deviation $(a - a_0)/a_0$. The dark green solid line shows corresponding analytic result [Eq. (7)], and the blue vertical dashed line shows the limit of the existence for this local minimum $[(a - a_0)/a_0 \leqslant 1/3]$.

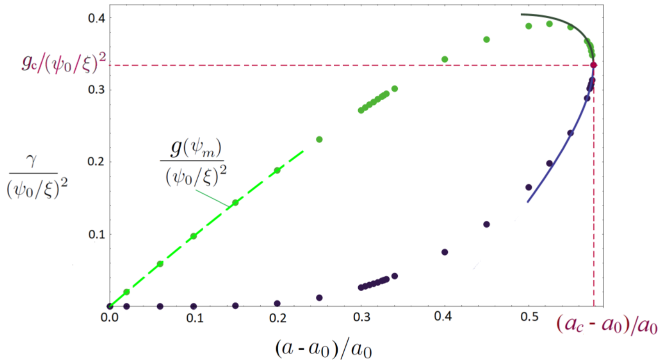

FIG. 2. Numerically found by solving Eqs. (29) and (30), using Eqs. (19) and (A2), values of γ_A for the Sm-*A* phase (dark blue circles) and γ_H for Hex-*B* phase (green circles) as a function of $(a - a_0)/a_0$. Light green dashed line represents the analytical dependence $g(\psi_m)/(\psi_0/\xi)^2$. Using Eqs. (B6) we fit the numerical data near the point $\gamma = g_c$. Dark blue solid lines are for the Sm-*A* phase ($\gamma \leqslant g_c$) and dark green for the Hex-*B* phase ($\gamma \geqslant g_c$).

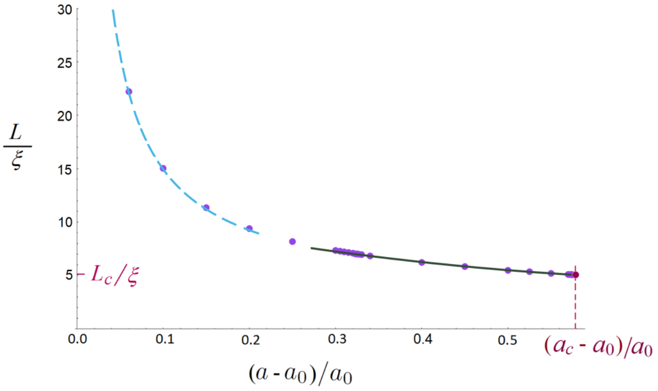

FIG. 3. Found numerically by solving Eqs. (29), (30), and (24) values of the dimensionless film thickness L/ξ in the coexistence regime (lilac circles) as a function of the dimensionless temperature deviation $(a - a_0)/a_0$. The azure dashed line in the left shows the corresponding analytic result [Eq. (A12)]. The green solid line [for $(a - a_0)/a_0 < (a_c - a_0)/a_0$] is obtained by fitting with Eq. (B5) the result near the point $\gamma = g_c$.

where we, again, extended the integration up to infinity due to convergence of the integral. Here the parameters in g_+ and ψ_A are taken at $T = T_+$ and the parameters in g_- and ψ_H are taken at $T = T_-$.

In our model, a is an L-dependent parameter in the coexistence region. Therefore we obtain from expression (10) $\alpha(T - T_+) + \beta(\mu - \mu_+) = 0$. This means $g_+ = g_- = g$, that is, $a_+ = a_- = a$ in the first order of the expansion of a over the deviations $(T - T_+)$, $(\mu - \mu_+)$. In this way, expanding the difference of the derivatives [Eq. (32)] over $T_+ - T_-$, $\mu_+ - \mu_-$ and using the condition, we find the relation

$$\frac{L\Gamma}{2\beta}(T_+ - T_-) + \int_{\psi_A}^{\psi_H} \frac{d\psi\ \psi^2}{\sqrt{g - \gamma_A}} + \int_{\psi_H}^{\infty} d\psi\ \psi^2 \left(\frac{1}{\sqrt{g - \gamma_A}} - \frac{1}{\sqrt{g - \gamma_H}} \right) = 0, \quad (33)$$

which determines the interval of the phase coexistence, see Fig. 5. The relation (33) can be rewritten as

$$\frac{L\Gamma}{\beta}(T_+ - T_-) + \frac{\partial \Delta\Phi}{\partial a} = 0, \quad (34)$$

as a consequence of Eq. (28). These relations [(33) and (34)] are our main results in the work, and they are ready for further inspection.

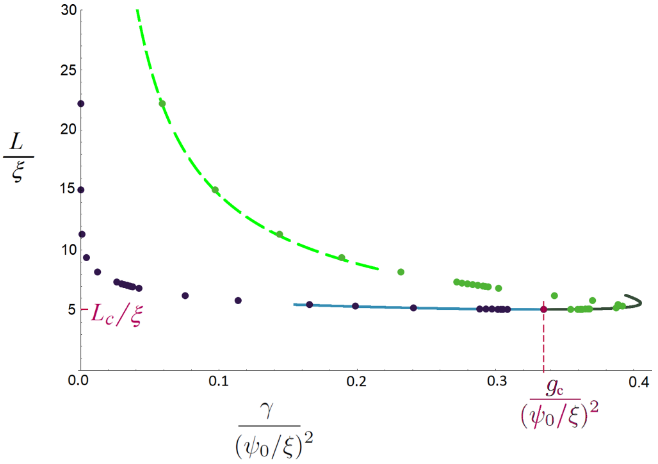

FIG. 4. Numerical values [found by solving Eqs. (29) and (30) with Eq. (24) and using Eqs. (19) and (A2)] for the dimensionless film thickness L/ξ in the coexistence regime of Sm-*A* (dark blue circles) and Hex-*B* phase (green circles) presented as a function of the dimensionless variable $\gamma/(\psi_0/\xi)^2$, in accordance with Fig. 2. The last right numerical point corresponds to the condition $\partial\gamma/\partial L = 0$. Corresponding analytical description according to the Eq. (A12), using Eq. (A2), is shown by the light green dashed line. Fitting [see Eqs. (B5) and (B6)] in the vicinity of the point $\gamma = g_c$ is shown by the blue solid line (for the Sm-*A* phase, $\gamma \leqslant g_c$) and by the dark green line (for the Hex-*B* phase, $\gamma \geqslant g_c$).

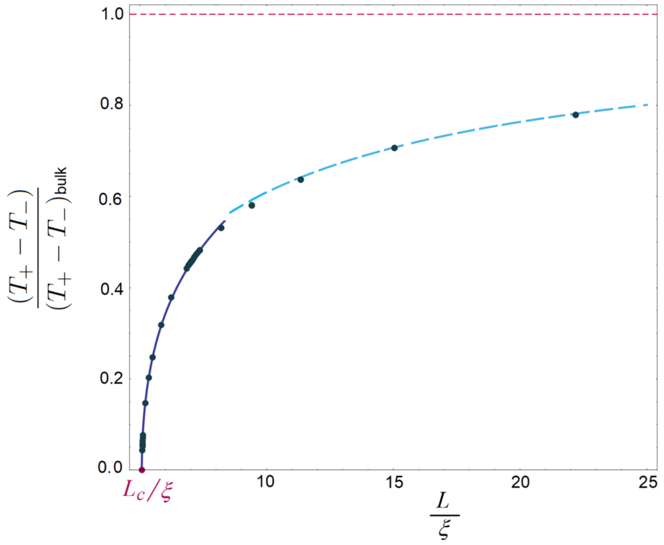

FIG. 5. The temperature interval of the phase coexistence as a function of the dimensionless film thickness L/ξ, computed by solving numerically Eqs. (29), (30), and (33) (dark blue points). Our theory result for the thick films [Eq. (A17)] is shown by the azure dashed line. The violet solid line (started from the point L_c/ξ) denotes the analytic solution to Eqs. (34), (46), (47), and (B5) in the vicinity of the point $a = a_c$.

Note that although L in smectic films must correspond to the integer number of discrete layers, in our macroscopic approach, for thick films one can treat L as a continuous variable.

C. Universal phase diagram

It is convenient to utilize the dimensionless variables a/a_0 and L/ξ. Then we obtain a universal picture, independent of the concrete values of the model parameters, from the results of the previous subsection. Despite the fact that the solution of the above nonlinear equations can be found only numerically, we can formulate some general universal laws valid (within our model assumptions) in the equilibrium phase coexistence region. Namely, the relations (24) imply that in the coexistence regime the equation $\Xi(a, \gamma) = L$ should have at least two solutions. Already this deceptively simple observation restricts the values of our model parameters. Let us first look at the function Ξ.

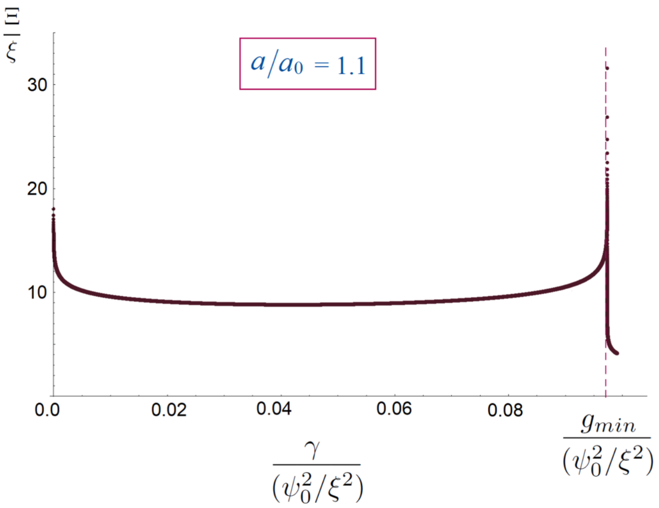

FIG. 6. Computed from Eq. (23) for $a/a_0 = 1.1$ (i.e., for the case $1 < a/a_0 < 4/3$) function Ξ/ξ versus $\gamma(\psi_0^2/\xi^2)^{-1}$.

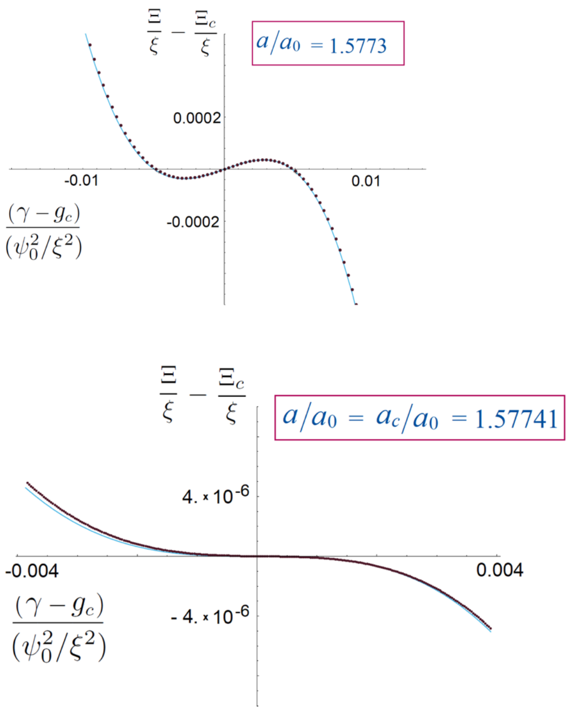

FIG. 8. Comparison of numerically found by solving Eq. (23) Ξ/ξ as a function of $(\gamma - g_c)(\psi_0^2/\xi^2)^{-1}$ with analytical approximation Eq. (B1) (thin azure solid line). $a/a_0 = 1.5773$ (i.e., for the case $a/a_0 > 4/3$) and $a/a_0 = a_c/a_0 = 1.57741$.

For small γ the function Ξ diverges logarithmically, see Fig. 6. If $1 < a/a_0 < 4/3$, then the function $g(\psi)$ (19) has a minimum at nonzero ψ. Therefore, the function Ξ logarithmically diverges at $\gamma \to g_{\min}$ where $g_{\min}$ is the minimal value of the function g. Thus Ξ has a minimum inside the interval $0 < \gamma < g_{\min}$, see Fig. 6. At $\gamma > g_{\min}$ the function Ξ monotonously decreases as γ grows. At $a/a_0 > 4/3$ the minimum in the function $g(\psi)$ disappears and Ξ becomes a regular function of γ. However, Ξ remains a nonmonotonic function of γ (it has a minimum and a maximum, see Figs. 7 and 8, up to some critical value a_c [and $\gamma(a_c) = g_c$], the value of a_c/a_0 is approximately equal to 1.5774, see Fig. 8). At $a > a_c$ the function $\Xi(\gamma)$ becomes monotonic.

Thus at $a < a_c$ there are three solutions of the equation $\Xi = L$ in some interval of the film thickness L. The smallest by the value of ψ solution corresponds to the Sm-*A* phase, $\gamma = \gamma_A$. The next by its ψ value solution corresponds to an unstable state. And, finally, the third solution with the biggest ψ corresponds to the Hex-*B* phase, $\gamma = \gamma_H$. In the limit $a \to a_c$ we find $\gamma_A \to \gamma_H$, and at $a > a_c$ there remains a single solution of the equation $\Xi(a, \gamma) = L$. Then the equilibrium phase coexistence region shrinks to zero. This result states that the equilibrium phase coexistence is possible only in the interval $a_0 < a < a_c$. Different values of a correspond to the different values of the film thickness L, see Fig. 3. The value of L_c/ξ is equal to 5.07.

D. Thick films

In this subsection we analyze the case of large film thickness, $L \gg \xi$. The limit has been discussed at the semiquantitatively level in Ref. [3]. Here we present the quantitative theory. For the thick films naturally the deviations of the film properties from the bulk ones are relatively small. In particular, the value of the parameter a is close to its bulk value a_0, $a - a_0 \ll a_0$. It follows from the relations (24) that at $L \gg \xi$ the integral (23) is anomalously large. It enables us to develop the consistent analytical procedure to study the surface effects in the equilibrium phase coexistence regime.

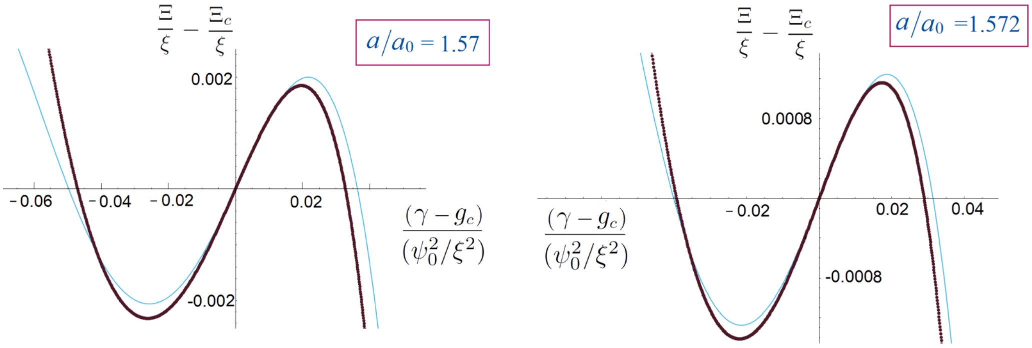

FIG. 7. Comparison of the numeric solution of Eq. (23) for Ξ/ξ as a function of $(\gamma - g_c)(\psi_0^2/\xi^2)^{-1}$ with our theory analysis [Eq. (B1)] (thin azure solid line). $a/a_0 = 1.57$ and $a/a_0 = 1.572$ (i.e., for the case $a/a_0 > 4/3$).

Let us turn to the hexatic phase. The value of ψ in the hexatic phase, ψ_H, is close to ψ_m, which corresponds to the minimum of g, see Eq. (7). The main contribution to the integral (23) stems from the vicinity of ψ_m. Near ψ_m the function g can be approximated as

$$g = \frac{\psi_0^2}{b}\left[a - a_0 + \frac{\lambda}{3}(\psi - \psi_m)^2\right]. \tag{35}$$

Starting from Eq. (35) and using Eqs. (23) and (24), we find with the logarithmic accuracy

$$\frac{L}{\xi} = \ln\frac{\psi_0}{\psi_H - \psi_m}. \tag{36}$$

Thus, $\psi_H - \psi_m$ is exponentially small in L/ξ.

Let us now turn to the Sm-*A* phase. At $L \gg \xi$ the main contribution to the integral (23) comes from the small ψ, where $g \approx a\psi^2/b$. Calculating the integral with the logarithmic accuracy, one obtains

$$L/\xi = 2\ln(\psi_0/\psi_A). \tag{37}$$

We conclude from Eq. (37) that ψ_A is exponentially small over L/ξ.

Now we use the condition $\Delta\Phi = 0$, see Eq. (25), to find a at a given L. We can substitute into Eq. (25) $\psi_A = 0$ and $\psi_H = \psi_m$. In the main approximation we obtain

$$\frac{a_0}{a - a_0} + \ln\frac{a_0}{a - a_0} = \frac{L}{\xi}. \tag{38}$$

We see that $(a - a_0)/a_0$ is a power of ξ/L that justifies the substitution $\psi_A \to 0$ and $\psi_H - \psi_m \to 0$ since the quantities are exponentially small.

Note that for the Sm-*A* phase there is an additional logarithmic contribution to the integral in Eq. (23), related to a vicinity of the minimum of $g(\psi)$, containing $\ln[a_0/(a - a_0)]$. As it follows from Eq. (38), the logarithm is $\ln(L/\xi)$. Therefore the contribution is irrelevant in comparison with L/ξ in the left-hand side of Eq. (37).

Now we rewrite Eq. (33) as

$$\begin{aligned}\frac{L\Gamma}{2\beta}(T_+ - T_-) &+ \int_0^{\psi_m} \frac{d\psi\,\psi^2}{\sqrt{g}}\\ &+ \int_{\psi_m}^{\infty} d\psi\,(\psi^2 - \psi_m^2)\left(\frac{1}{\sqrt{g}} - \frac{1}{\sqrt{g - \gamma_H}}\right)\\ &+ \psi_m^2\int_{\psi_m}^{\infty}\frac{d\psi}{\sqrt{g}} - \psi_m^2\int_{\psi_m}^{\infty}\frac{d\psi}{\sqrt{g - \gamma_H}} = 0,\end{aligned} \tag{39}$$

where we substituted $\psi_A = 0$, $\psi_H = \psi_m$. The last term in Eq. (39) is equal to $\psi_m^2 L/2$, in agreement with Eq. (24).

In the main approximation we find

$$\frac{\Gamma}{\beta\psi_0^2}(T_+ - T_-) = 1 - \frac{\xi}{L}\ln\frac{L}{\xi}, \tag{40}$$

where we used Eq. (38). The expression (40) gives the first correction to the bulk expression (14). The contributions leading to the logarithmic factor in Eq. (40) were missed in Ref. [3]. Therefore, the expression for the temperature width of the phase coexistence region presented in Ref. [3] can be used only for qualitative interpretation of the data. Note, however, that in terms of numeric values for the range of the film thicknesses considered in Ref. [3], the logarithmic factor is almost irrelevant. Nevertheless, the logarithmic factor is very important conceptually. Thanks to this factor we are in the position to perform consistently our calculations with logarithmic accuracy (see the Appendices where higher-order corrections included). This allows us to distinguish the above-determined law for the temperature width of the coexistence region from regular (existing in any system) finite-size corrections which scale as ξ/L. The fact that ψ_A and $\psi_H - \psi_m$ are exponentially small enables us to find analytically the next terms of the expansion over the parameter ξ/L in the expression for $T_+ - T_-$. The corresponding analysis is shown in Appendix A; see also Figs. 3 and 4.

E. Thin films

For thin films, we consider the case $a > 4/3a_0$. Then the quantity Ξ (23) has no singularities as a function of γ. However, at $a < a_c$ it is still a nonmonotonic function of γ. At $a = a_c$ the function Ξ (23) has a point $\gamma = g_c$, where both $\partial\Xi/\partial\gamma$ and $\partial^2\Xi/\partial\gamma^2$ are equal to zero.

In the vicinity of the point the quantity Ξ can be approximated as

$$\frac{\Xi}{\xi} = \frac{\Xi(a, y_c)}{\xi} - A(y - y_c)^3 - B\frac{a - a_c}{a_0}(y - y_c), \tag{41}$$

where $y = \gamma(\psi_0^2/\xi^2)^{-1}$ and A, B are dimensionless constants. Their numerical values are $A = 82.1362$, $B = 17.6392$. Exploiting Eq. (26), one finds from Eq. (41)

$$\begin{aligned}\frac{\xi\Delta\Phi}{\psi_0^2} &= \left[\frac{\Xi(a, y_c)}{\xi} - \frac{L}{\xi}\right](y_H - y_A)\\ &\quad - \frac{A}{4}[(y_H - y_c)^4 - (y_A - y_c)^4]\\ &\quad - \frac{B}{2}\frac{a - a_c}{a_0}[(y_H - y_c)^2 - (y_A - y_c)^2].\end{aligned} \tag{42}$$

Now we can find the equilibrium values of the parameters that are determined by the conditions (24) and $\Delta\Phi = 0$. The conditions (24) are written as

$$\begin{aligned}&\Xi(a, y_c)/\xi - L/\xi\\ &\quad = A(y_H - y_c)^3 + B\frac{a - a_c}{a_0}(y_H - y_c)\\ &\quad = A(y_A - y_c)^3 + B\frac{a - a_c}{a_0}(y_A - y_c).\end{aligned} \tag{43}$$

Equating then $\Delta\Phi$ to zero, we find from Eqs. (42) and (43)

$$L = \Xi(a, y_c), \tag{44}$$

$$\begin{aligned}y_H - y_c &= \sqrt{B(a_c - a)/(Aa_0)},\\ y_A - y_c &= -\sqrt{B(a_c - a)/(Aa_0)}.\end{aligned} \tag{45}$$

Thus the equilibrium branch of the curve $y_A(a)$, $y_H(a)$ near the point a_c, y_c is a parabola.

Since in the equilibrium the derivatives of $\Delta\Phi$ over $\gamma_A = (\psi_0^2/\xi^2)y_A$ and $\gamma_H = (\psi_0^2/\xi^2)y_H$ are zero, we find in the main

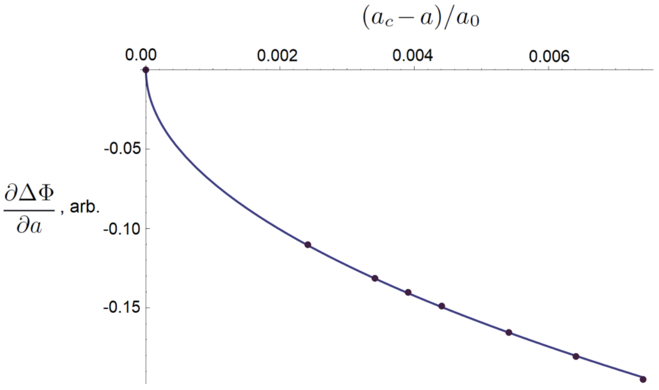

FIG. 9. Comparison of our numeric results [solution to Eq. (28) for $\partial\Delta\Phi/\partial a$ versus $(a_c - a)/a_0$] in the coexistence regime (dark blue circles) with analytic theory [Eq. (47)] near the point $a = a_c$ (blue solid line).

approximation from Eq. (42)

$$\frac{\partial \Delta\Phi}{\partial a} = 2\frac{\psi_0^2}{\xi^2}\frac{\partial \Xi}{\partial a}\sqrt{\frac{B(a_c - a)}{A a_0}} \tag{46}$$

at the equilibrium curve. Here the derivative $\partial\Xi/\partial a$ is taken at $y = y_c$. We conclude that

$$\frac{\partial \Delta\Phi}{\partial a} \propto (a_c - a)^{1/2}, \tag{47}$$

that is, the derivative tends to zero as $a \rightarrow a_c$, see Fig. 9. Thus, in the agreement with Eqs. (34) the width of the equilibrium phase coexistence region shrinks, $T_+ - T_- \propto (a_c - a)^{1/2}$ as $a \rightarrow a_c$, see Figs. 5 and 10. A similar procedure can be used to calculate the higher-order terms over $a - a_c$, $y - y_c$ to the expansion (41). Technical details and final results are presented in Appendix B; see also Figs. 2, 3, and 4.

IV. CONCLUSION

In summary, we developed the theory describing thermodynamic features of the free-standing smectic films in the temperature range where the equilibrium phase coexistence Sm-*A*-Hex-*B* occurs. Our results explain how the surface-induced ordering reduces the width of the equilibrium phase coexistence region. Quite remarkably, the width shrinks to zero when the film thickness L becomes of the order of a few hexatic correlation length along the z axis. The behavior of the film at $L \rightarrow L_c$ resembles the classical gas-liquid critical point, where the coexisting phases become indistinguishable. Our analysis of the surface-bulk ordering interplay predicts universal laws for the equilibrium phase coexistence range in terms of the reduced parameters. The described phenomena and the calculated specific relations between the parameters are our main predictions. They depend only on a few dimensionless parameters. Thus we arrived at the universal picture in terms of the reduced parameters.

Let us stress that our crucial assumption, that the Sm-*A*-Hex-*B* transition is close to the tricritical point, is strongly supported by the existing experimental data [3,16–18,21], which demonstrate weak first-order phase transitions. Moreover, the measured critical exponents (for the specific heat and for the order parameter) are close to those for the tricritical point [16–18,21]. Therefore our theory is applicable to all such materials, and our predictions (the finite-temperature range for the equilibrium phase coexistence, the film thickness as the parameter governing the width of the coexistence region, and universal laws for the width dependence on the system parameters) hold.

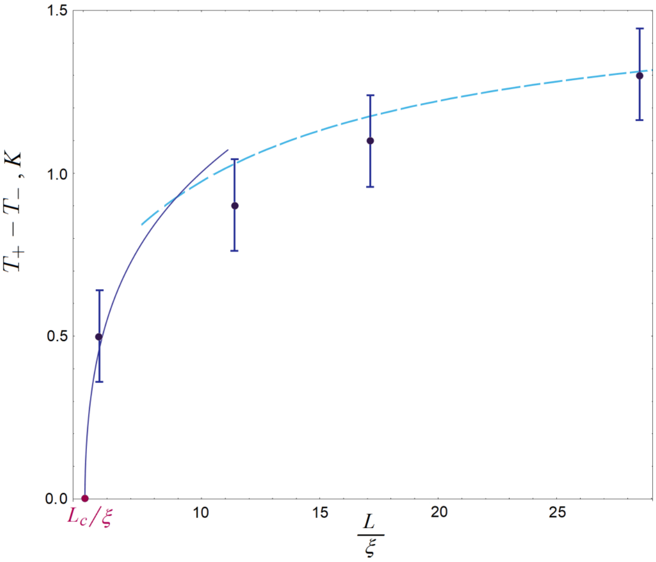

FIG. 10. Experimental data, borrowed from Ref. [3], on the temperature range ΔT of the Sm-*A* and Hex-*B* phase coexistence as a function of the dimensionless film thickness L/ξ (on cooling, shown by dark blue circles). Our analytical description of the data by Eq. (A17) for the thick films is shown by the azure dashed line. In numeric computation we used the following fitting parameters: $\xi = 3.5 \times 10^{-7}$ m and $\beta\psi_0^2/\Gamma = 1.6$. Our results near the point $a = a_c$ (the violet solid line) are plotted by solving Eqs. (34), (46), (47), and (B5).

We neglected fluctuations of the order parameter. It is well known that near the tricritical point fluctuations provide logarithmic corrections to the mean-field values. Since, in accordance with our scheme, in the range of the equilibrium phase coexistence the control parameter a varies in a relatively narrow interval (on the order of the bulk value a_0), the logarithmic renormalization of the coefficients is not essential for our consideration. However, when the film thickness approaches the critical value L_c, the smectic and hexatic states become indistinguishable, signaling a special critical point. This special critical point is basically similar to the conventional liquid-gas critical point, where fluctuations of the two-component hexatic order parameter (modulus and phase) are relevant (see Refs. [39,40] in addition to Refs. [22–24]). We defer investigation of this point for a future work.

To illustrate how our theory works, we reanalyze the experimental data presented in Ref. [3] for the Sm-*A*-Hex-*B* coexistence in the free-standing film of the 54COOBC material. Measured in Ref. [3] the temperature width ΔT of the phase coexistence region at different film thickness can be reasonably described by our theory. The comparison suggests also that these experimental data correspond to the regime of the intermediate film thicknesses (between described analytically the thick- and thin-film limits). We presented in Fig. 10 our analytical description of Eqs. (A17), (34), (46), (47), and (B5) of the experimental data on the temperature range ΔT of the Sm-*A* and Hex-*B* phase coexistence from Ref. [3].

In this work we investigated the Sm-*A*-Hex-*B* phase transition in the vicinity of the tricritical point, characterized by the two-component (complex) order parameter. Generally, our theory can be applied to other orientation phase transitions in smectics, provided the state is close to a tricritical point. For example, it is applicable to the transition between the untilted Sm-*A* and the tilted Sm-*C* states. However, the explicit expressions require some modifications. Namely, one has to include the uniaxial orientational anisotropy within the smectic layers (to compare with the hexagonal symmetry of the *HexB* layers) and, more importantly, induced by cooperative molecular tilting, the layer thickness variation at the transition.

Our theory can be also adjusted to describe the paraelectric-ferroelectric phase transitions in solid films, where the transition is close to a tricritical point (see, e.g., Refs. [41,42] for the case of thin ceramic ferroelectric films). Furthermore, for the thin ferroelectric films surface ordering occurs prior yo the bulk one, and it yields to a critical point, mentioned in Refs. [43–45]. To modify our theory for the ferroelectric solid films, one has to include elastic energy, long-range dipolar forces, domain structures, and so on. Note also that the equilibrium phase coexistence, tricritical behavior, and the film finite-thickness effects are very common in nature, not only for the smectics or the ferroelectrics but also for spin-density waves, charge density waves, and adsorbed atoms.

A remarkable peculiarity of the Landau theory is that it is a powerful tool for description of different systems in terms of the order parameter irrespective of its microscopic nature. The system properties depend solely on the system dimension, symmetry, and the number of the components of the order parameter. Similarity in the description can be even more close if one considers quasi-two-dimensional layered structures, such as high-temperature superconductors with puzzling properties. One more remark can be useful here. The matter is that in the smectic liquid crystals, unlike superconductors and superfluids, not only do both components of the order parameter have a transparent physical nature, but also the fields conjugated to the modulus and to the phase have realistic physical sources (e.g., uniaxial pressure and electric or magnetic fields). This cannot be said about a superconducting gap and superfluid density for which there is no conjugated physical field. It is tempting to use smectic phases for modeling of different unusual superstructures forming in superconductors and superfluids. To the same point, the interplay between surface and bulk order we found in this work in smectic films recently has become very popular with a number of fascinating applications in several branches of physics, like holographic principles in high-energy physics or in topological insulators (see, e.g., Refs. [46,47]).

ACKNOWLEDGMENTS

This work was inspired by recent x-ray studies of the Sm-*A* and Hex-*B* phase coexistence in free-standing smectic films [3]. We are grateful to all members of the experimental team for providing us with the very first results of their remarkable observations. Special thanks are due to B. I. Ostrovskii, I. A. Vartanyants, I. A. Zaluzhnyy, and R. P. Kurta for stimulating discussions. The reported study was supported by the Ministry of Science and Higher Education of the Russian Federation within the State assignment (Theme No. 0033-2019-0003). The contribution of E.S.P. connecting with numerical investigation of smectic films of intermediate thicknesses was supported by the Russian Science Foundation (Grant No. 18-12-00108).

APPENDIX A

Here we analyze the case of thick films, $L \gg \xi$. Then a is close to a_0. The system of equations can be stated in a more elegant form (ready for numerics) by introducing dimensionless variables,

$$\varpi = a/a_0 - 1, \quad x = \psi^2/\psi_0^2, \tag{A1}$$

and one obtains

$$g = (\psi_0/\xi)^2 x(1 + \varpi - 2x + x^2). \tag{A2}$$

The parameter $\varpi > 0$ is small for our case. The quantity g (A2) has the minimum at $x = x_m$, where

$$x_m = \frac{2}{3}\left(1 + \frac{1}{2}\sqrt{1 - 3\varpi}\right) < 1. \tag{A3}$$

As we explained, in the case $L/\xi \gg 1$ both ψ_A and $\psi_H - \psi_m$ are exponentially small over L/ξ. Therefore, to analyze effects, with a power law over ξ/L dependence, one can put $\psi_A = 0$, $\psi_H = \psi_m = \psi_0\sqrt{x_m}$. Then one finds from Eq. (22)

$$\frac{\xi}{b\psi_0^2}\Phi_A = \varphi_A, \tag{A4}$$

$$\frac{\xi}{b\psi_0^2}\Phi_H = 2x_m^2(1 - x_m)\frac{L}{\xi} + \varphi_H. \tag{A5}$$

The dimensionless quantities φ_A and φ_H are defined as

$$\begin{aligned}\varphi_A &= 2\int_0^s dx\sqrt{x^2 - 2x + 1 + \varpi}\\ &= (s-1)(s^2 - 2s + 1 + \varpi)^{1/2} + \sqrt{1+\varpi}\\ &\quad - \varpi\ln\frac{1 - s + (s^2 - 2s + 1 + \varpi)^{1/2}}{1 + \sqrt{1+\varpi}}\end{aligned} \tag{A6}$$

and

$$\begin{aligned}\varphi_H &= 2\int_{x_m}^s \frac{dx}{\sqrt{x}}\sqrt{x - 2(1 - x_m)}\,(x - x_m)\\ &= (s - x_m - 1)\sqrt{s(s - 2 + 2x_m)} + \sqrt{x_m(3x_m - 2)}\\ &\quad + 2\varpi\ln\frac{\sqrt{s} + \sqrt{s - 2(1 - x_m)}}{\sqrt{x_m} + \sqrt{3x_m - 2}},\end{aligned} \tag{A7}$$

where s stands for the surface value of the order parameter.

Using Eqs. (A6) and (A7), one can easily calculate

$$\begin{aligned}\lim_{s\to\infty}(\varphi_A - \varphi_H) &= \sqrt{1+\varpi} - \sqrt{x_m(3x_m - 2)}\\ &\quad + x_m - \varpi\ln\frac{2(\sqrt{1+\varpi} - 1)}{(\sqrt{x_m} + \sqrt{3x_m - 2})^2}.\end{aligned} \tag{A8}$$

Therefore the condition $\Delta\Phi = 0$ reads as

$$\begin{aligned}\sqrt{1+\varpi} - \sqrt{x_m(3x_m-2)} + x_m \\ -\varpi \ln \frac{2(\sqrt{1+\varpi}-1)}{(\sqrt{x_m}+\sqrt{3x_m-2})^2} \\ = 2x_m^2(1-x_m)\frac{L}{\xi}.\end{aligned} \tag{A9}$$

This equation relates ξ/L and ϖ.

Now we turn to the relation (39), which can be rewritten as

$$\begin{aligned}\frac{\Gamma}{\beta\psi_0^2}(T_+ - T_-) + \frac{\xi}{L}\int_0^s \frac{dx}{\sqrt{x^2-2x+1+\varpi}} \\ -\frac{\xi}{L}\int_{x_m}^s \frac{dx}{\sqrt{x^2-2(1-x_m)x}} - x_m = 0.\end{aligned} \tag{A10}$$

The integrals here are

$$\int_0^s \frac{dx}{\sqrt{x^2-2x+1+\varpi}} = \ln \frac{s-1+\sqrt{s^2-2s+1+\varpi}}{\sqrt{1+\varpi}-1},$$

$$\int_{x_m}^s \frac{dx}{\sqrt{x^2-2(1-x_m)x}} = 2\ln \frac{\sqrt{s}+\sqrt{s-2+2x_m}}{\sqrt{x_m}+\sqrt{3x_m-2}}.$$

Substituting the expressions into Eq. (A10) and passing to the limit $s \to \infty$, one obtains

$$\frac{\Gamma(T_+-T_-)}{\beta\psi_0^2} + \frac{\xi}{L}\ln\frac{(\sqrt{x_m}+\sqrt{3x_m-2})^2}{2(\sqrt{1+\varpi}-1)} = x_m. \tag{A11}$$

The equation relates ξ/L and $T_+ - T_-$.

The expressions (A3), (A9), and (A11) admit a regular expansion over ϖ. Keeping zero and first terms of the expansion, we get

$$\frac{1}{\varpi} + \ln\frac{4}{\varpi} + \frac{5}{4} = \frac{L}{\xi}, \tag{A12}$$

$$\frac{\Gamma(T_+-T_-)}{\beta\psi_0^2} = \frac{\xi}{L\varpi} + \frac{\xi}{L} - \frac{\varpi}{4}. \tag{A13}$$

Taking into account only the main logarithmic term, we reproduce Eqs. (38) and (40). In the next order over ϖ one finds the relations

$$\frac{1}{\varpi} + \left(1+\frac{\varpi}{4}\right)\ln\frac{4}{\varpi} + \frac{5}{4} + \frac{\varpi}{16} = \frac{L}{\xi}, \tag{A14}$$

$$\frac{\Gamma(T_+-T_-)}{\beta\psi_0^2} = \frac{\xi}{L\varpi} + \frac{\xi}{L} + \frac{3\varpi}{8}\frac{\xi}{L} - \frac{\varpi}{4} - \frac{\varpi^2}{4}. \tag{A15}$$

Expressing ϖ via ξ/L from Eq. (A14), we obtain in the same approximation

$$\begin{aligned}\varpi = \frac{\xi}{L} + \left(\frac{\xi}{L}\right)^2\left(\ln\frac{4L}{\xi}+\frac{5}{4}\right) \\ + \left(\frac{\xi}{L}\right)^3\left[\left(\ln\frac{4L}{\xi}\right)^2 + \frac{7}{4}\ln\frac{4L}{\xi} + \frac{3}{8}\right],\end{aligned} \tag{A16}$$

the function L/ξ versus ϖ is presented in Fig. 3. Substituting the expression (A16) into Eq. (A15), we finally find

$$\begin{aligned}\frac{\Gamma(T_+-T_-)}{\beta\psi_0^2} = 1 - \frac{\xi}{L}\left(\ln\frac{4L}{\xi}+\frac{1}{2}\right) \\ + \left(\frac{\xi}{L}\right)^2\left(\frac{1}{2}\ln\frac{4L}{\xi}+1\right),\end{aligned} \tag{A17}$$

in the second order over ξ/L. We plot the corresponding dependence of $T_+ - T_-$ on the dimensionless film thickness L/ξ in Fig. 5.

APPENDIX B

Here we analyze in more detail the case where L is close to L_c and the coexistence region is rather narrow in its width. Then one should start from the expression (41), correct near the point a_c, y_c. We discuss next corrections to the expression (41). The modified expression can be written as

$$\begin{aligned}\frac{\Xi}{\xi} = \frac{\Xi(a,y_c)}{\xi} - A(y-y_c)^3 - B\frac{a-a_c}{a_0}(y-y_c) \\ + C(y-y_c)^4 + D\frac{a-a_c}{a_0}(y-y_c)^2,\end{aligned} \tag{B1}$$

$$\frac{\Xi(a,y_c)}{\xi} = \frac{\Xi_c}{\xi} + A_1\frac{a-a_c}{a_0} + B_1\left(\frac{a-a_c}{a_0}\right)^2, \tag{B2}$$

where A, B, D, C, A_1, and B_1 are dimensionless parameters. The corrections with the coefficients C and D contain an extra power of $y - y_c$ in comparison with the main terms with the coefficients A and B. The parameters D, C, A_1, and B_1 can be found numerically, and they are $D = -45.6325$, $C = -724.459$, $A_1 = -4.81157$, and $B_1 = 14.4096$.

The next step is to generalize Eq. (42)

$$\begin{aligned}\frac{\xi\Delta\Phi}{\psi_0^2} = \left[\frac{\Xi(a,y_c)}{\xi} - \frac{L}{\xi}\right](y_H - y_A) \\ - \frac{A}{4}[(y_H-y_c)^4 - (y_A-y_c)^4]\end{aligned}$$

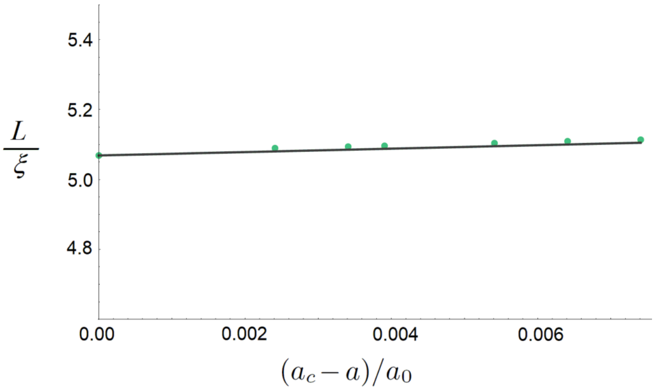

FIG. 11. Comparison of the numeric results for L/ξ (light green circles) versus $a_c - a$ with their analytic counterparts given by Eq. (B5) near the point $a = a_c$. Branch corresponding to the Eq. (B5) is shown by the dark green solid line.

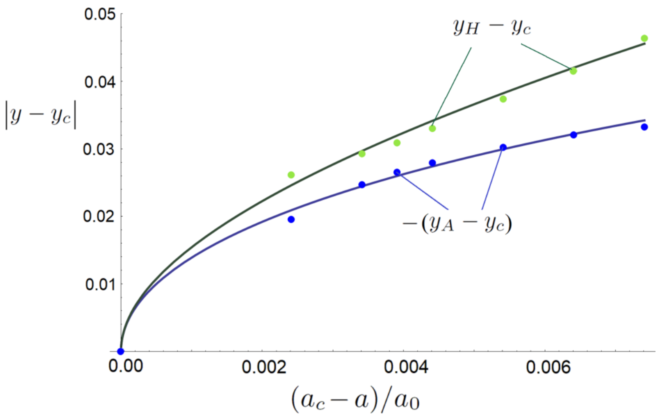

FIG. 12. Comparison of the numeric results for $y_H - y_c$ (light green circles) and $-(y_A - y_c)$ (blue circles) versus $a_c - a$ with analytic ones given by Eqs. (B6) near the point $a = a_c$. Curves corresponding to the Eqs. (B6) are shown by the solid lines (upper dark green for Hex-B phase and bottom blue for Sm-A).

$$-\frac{B}{2}\frac{a-a_c}{a_0}[(y_H-y_c)^2-(y_A-y_c)^2] + \frac{C}{5}[(y_H-y_c)^5-(y_A-y_c)^5] + \frac{D}{3}\frac{(a-a_c)}{a_0}[(y_H-y_c)^3-(y_A-y_c)^3]. \tag{B3}$$

Now we can find the equilibrium values of the parameters that are determined by the conditions (24) and $\Delta\Phi = 0$. The conditions (24) are written as

$$\begin{aligned}\Xi(a, y_c)/\xi - L/\xi &= A(y_H-y_c)^3 + B\frac{(a-a_c)}{a_0}(y_H-y_c) - C(y_H-y_c)^4 - D\frac{a-a_c}{a_0}(y_H-y_c)^2 \\ &= A(y_A-y_c)^3 + B\frac{a-a_c}{a_0}(y_A-y_c) - C(y_A-y_c)^4 - D\frac{a-a_c}{a_0}(y_A-y_c)^2.\end{aligned} \tag{B4}$$

The expressions generalize Eq. (43). The condition $\Delta\Phi = 0$ gives the equation following from Eq. (B3).

To have a regular expansion (perturbation theory) we assume the higher-order corrections to be small. Then we find after substitution of (B4) to condition $\Delta\Phi = 0$

$$\frac{L}{\xi} - \frac{\Xi(a, y_c)}{\xi} = \left(\frac{C}{5} - \frac{DA}{3B}\right)\left(\frac{B(a-a_c)}{Aa_0}\right)^2, \tag{B5}$$

$$y_H, y_A = y_c \pm \sqrt{\frac{B(a_c-a)}{Aa_0}} - \left(\frac{3C}{5A} - \frac{2D}{3B}\right)\frac{B}{A}\frac{a-a_c}{a_0}, \tag{B6}$$

instead of Eqs. (44) and (45). The applicability condition of the expressions implies that the corrections to y_H, y_A are small in comparison with the main contribution. Comparing the expression (B5) with Eq. (B2), we conclude that L is expanded over integer powers of $(a - a_c)/a_0$. Our numeric results, shown in Figs. 11 and 12, are in agreement with the above-presented analytic expansion, see Eqs. (B5) and (B6).

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