

First-order Landau–de Gennes model for layer thinning in presmectic free-standing films

D. E. Sullivan

Department of Physics and Guelph-Waterloo Physics Institute, University of Guelph, Guelph, Ontario, Canada N1G 2W1

A. N. Shalaginov

EMC Corporation, Hopkinton, Massachusetts 01748, USA

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A Landau theory for surface enhanced ordering in free-standing smectic-A films is described, based on a generalization of de Gennes’s “presmectic” model to systems which undergo a first-order smectic-isotropic transition in bulk. As found in related work on phase transitions in thin films, the system exhibits three phases, an isotropic liquid, a bulk-like ordered (smectic-A) phase, and a surface-ordered (“quasismectic”) phase. Over much of its range, the temperature-thickness boundary between the bulk-ordered and surface-ordered phases is effectively characterized by a power-law relation similar to those observed for layer-thinning transitions in overheated free-standing smectic-A films.

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I. INTRODUCTION

Layer-thinning transitions in overheated free-standing films of certain smectic-A liquid crystals were discovered nearly ten years ago by Huang *et al.* [1–3]. Several mean-field theories for these transitions have been described [4–10]. Common features of all these theories are the existence of enhanced smectic-A ordering at the free surfaces of a film and the fact that thinning occurs when the smectic ordering in the interior of a film becomes sufficiently weak. Apart from details of the models used, the main differences between the various theories are in the description of the kinetic pathways by which layer thinning occurs, i.e., whether this is by uniform squeezing-out of the melted interior [4–8] or via nucleation of dislocation loops between domains of differing thickness [9,10] (a scenario supported by experimental studies [11,12]). Many of the previous theoretical studies of layer-thinning transitions [7–11,13] have been based on de Gennes’ model of “presmectic” ordering in thin films [14]. Up to now, all of the latter studies use an expansion of the bulk free-energy density up to at most quartic order in the smectic order parameter, which is more appropriate to a system undergoing a *second-order* smectic-nematic phase transition. In contrast, the majority of experimental studies of layer-thinning transitions have been done on systems exhibiting first-order smectic-isotropic transitions in bulk [1–3,11,12]. In this paper we extend our previous studies [8,10], based on a modified version of de Gennes’ presmectic theory which included a quartic term in the bulk free-energy density and a quadratic (rather than linear) term in the surface part of the free energy, by adding a sixth-order term to the bulk free-energy density so as to be applicable to systems with first-order bulk transitions. Here we limit the analysis to determining the different phases and their “equilibrium” boundaries exhibited by a thin presmectic film in the absence of layer strain effects.

The theory discussed here is closely related to one described a few years ago by Weinstein and Safran [15] in the context of freezing transitions in confined liquid films. Earlier work employing a similar formalism [16,17] examined

confinement effects on the first-order nematic-isotropic transition. The study in Ref. [17] is important for relating the predicted thin-film phase boundaries to the interplay of capillary condensation and wetting phenomena. In the presence of surface-enhanced ordering, these studies all find that three types of phases can occur in a confined film in a range of temperatures T above the bulk transition temperature, denoted T_x : (1) a mainly isotropic state with little or no ordering at both the interfaces and interior of the film; (2) a “bulk-ordered” state which exhibits significant ordering throughout the film; and (3) a “surface-ordered” state in which the film interfaces are wet by the ordered phase while the middle of the film is very weakly ordered. In the context of free-standing smectic films, the latter has been called a “quasismectic” state [4], although this behavior probably is rather generic for a confined film with a sufficient degree of surface-enhanced ordering. The transition between states (1) and (2) in a film of finite thickness L is the analog of capillary condensation between gas-like and liquid-like states in a confined geometry [18]. The phase boundary between these states, in terms of temperature and thickness, is described asymptotically by the Kelvin relation $L \propto \Delta T^{-1}$ where $\Delta T \equiv T - T_x$. For sufficiently small ΔT , the surface-ordered phase (3) becomes more stable than the isotropic phase and the (1)–(2) transition is preempted by the (2)–(3) transition. Although *asymptotically* this phase boundary also obeys the Kelvin relation, over a wide range we find that it is characterized by an effective power law $L \propto \Delta T^{-\nu}$ with ν as small as 0.76, which is consistent with the L – T relations observed in layer-thinning transitions [1–3,11]. This finding, along with demonstrating the “universal” character of the quasismectic state and its connections to other confinement-induced transitions, are the main points of this paper.

II. MODEL

As in previous work [7–11,13] employing de Gennes’ presmectic model [14], a free-standing smectic-A film is modeled by an infinite liquid slab parallel to the (x, y) plane

with free liquid-vapor interfaces at $z=\pm L/2$. The degree of smectic order in the film is described by the order parameter $\psi(z)\geq 0$, representing the amplitude of periodic density modulations in the normal z direction. The model neglects any explicit coupling to a nematic-like orientational order parameter, on the assumption [11] that any such order is fully saturated as soon as it develops. As stated by de Gennes [14], such a model should be applicable to systems exhibiting either a nematic or isotropic phase in bulk. As mentioned in Sec. I, here we will neglect strain effects associated with local distortions of the smectic layer thickness. This is justified by the expectation, indicated by previous work [7,8,14], that the minima in the free energy lie close to states of zero strain. The Landau-de Gennes free energy per unit area of the film, accounting for the effects of smectic ordering, is then given by

$$F = \int_{-L/2}^{L/2} dz \left[f_b(\psi) + \frac{C}{2} \left(\frac{d\psi}{dz} \right)^2 \right] + f_s[\psi(L/2)] + f_s[\psi(-L/2)]. \quad (1)$$

As appropriate for a system undergoing a first-order smectic-isotropic transition, the bulk free-energy density $f_b(\psi)$ is given by [19]:

$$f_b(\psi) = \frac{r}{2} \psi^2 - \frac{b}{4} \psi^4 + \frac{g}{6} \psi^6, \quad (2)$$

where b and g are positive constants. As usual, the variable r is taken to be linear in the relative temperature difference, i.e., $r \propto T - T_0$, where T_0 is a supercooling spinodal temperature. In the following, we will often simply call r the ‘‘temperature.’’ Our model for the contribution $f_s(\psi)$ to the free energy, which accounts for the smectic ordering effects of the film surfaces on adjacent molecules, is [8,10]:

$$f_s(\psi) = \frac{g_s}{2} \psi^2, \quad (3)$$

where g_s is a surface coupling constant. This model neglects a possible contribution to f_s in which is linear in ψ [8,13]. By analogy with related studies, e.g., on Ising-model surfaces [20], a linear term in f_s would be associated with *external* fields such as due to confining walls acting on the film, expected to be absent in a free-standing film, while the quadratic form adopted in Eq. (3) accounts for the effects of modified intermolecular pair interactions (e.g., ‘‘missing neighbors’’) near the surface. In other contexts [20], g_s has been called the ‘‘surface-enhancement field,’’ which favors local ordering at the interfaces when $g_s < 0$, a condition which is assumed from now on. The form of f_s in Eq. (3) is simpler than that used in Ref. [15], which also neglected the linear term. Along with the neglect of nematic ordering terms elsewhere in F , the form of the surface free energy assumes that any explicit orientational anchoring effects can be eliminated in terms of the smectic order parameter ψ . This is reasonable under the conditions that molecules at the surface remain homeotropically aligned (i.e., normal to the surface), compatible with smectic-*A* ordering parallel to the surface [9,14]. By appropriate scaling of F , ψ , and z , the coefficients

b , g , and C in Eqs. (1) and (2) can be set equal to unity [21], as adopted from now on. This leaves the model depending on two parameters, the temperature variable r and the surface coupling constant g_s .

Euler-Lagrange equations determining the order-parameter profile $\psi(z)$ along with the surface value $\psi(\pm L/2)$ can be obtained by functional minimization of Eq. (1). We will omit these equations here, and simply state that on using these equations and the symmetry condition $\psi(-z) = \psi(z)$, Eq. (1) becomes [16,17]:

$$F = f_b(\psi_0)L + 2f_s(\psi_s) + 2\sqrt{2} \int_{\psi_0}^{\psi_s} d\psi [f_b(\psi) - f_b(\psi_0)]^{1/2}, \quad (4)$$

where $\psi_0 \equiv \psi(z=0)$ is the order parameter in the midplane of the film while $\psi_s \equiv \psi(z=\pm L/2)$ is the order parameter at the film surfaces. In this form, F can be considered a function of the three variables ψ_0 , ψ_s , and film thickness L , for given model parameters r and g_s . Partial minimization of F in Eq. (4) with respect to ψ_s and ψ_0 , respectively, using Eq. (3), yields the relations

$$\sqrt{2} [f_b(\psi_s) - f_b(\psi_0)]^{1/2} = -g_s \psi_s, \quad (5)$$

and

$$L = G(\psi_0), \quad (6a)$$

where

$$G(\psi_0) = \sqrt{2} \int_{\psi_0}^{\psi_s} \frac{d\psi}{[f_b(\psi) - f_b(\psi_0)]^{1/2}}. \quad (6b)$$

These relations can also be obtained from the original Euler-Lagrange equations for $\psi(z)$. If one considers Eq. (5) as determining the surface order parameter ψ_s in terms of the mid-film value ψ_0 , then Eqs. (6a) and (6b) determine ψ_0 for a given thickness L , where $\psi_s = \psi_s(\psi_0)$ in the upper limit of the integral defining the function $G(\psi_0)$ in Eq. (6b). In view of the latter equations, the *total* derivative of F with respect to the film thickness L (at fixed r and g_s) is given by

$$\frac{dF}{dL} = \left(\frac{\partial F}{\partial L} \right)_{\psi_0, \psi_s} = f_b(\psi_0). \quad (7)$$

An alternative expression for the equilibrium free energy which can be obtained using the Euler-Lagrange equations for $\psi(z)$, following an approach described in Ref. [8], is

$$F = \int_0^{L/2} dz \left[2f_b(\psi) - \psi \frac{\partial f_b(\psi)}{\partial \psi} \right] + 2f_s(\psi_s) - \psi_s \frac{\partial f_s(\psi_s)}{\partial \psi_s}. \quad (8)$$

Using the forms of f_b and f_s in Eqs. (2) and (3), this becomes

$$F = \int_0^{L/2} dz \psi^4(z) \left[\frac{1}{2} - \frac{2}{3} \psi^2(z) \right]. \quad (9)$$

Although not generally as useful as Eq. (4), this indicates that the free energy F is necessarily positive if $\psi(z) < \sqrt{3/4}$ for all z .

Before discussing the solutions of Eqs. (5), (6a), and (6b), we point out some relevant features of the bulk free-energy density $f_b(\psi)$. Close to the bulk isotropic-smectic transition, this has a characteristic “double well” shape, having one minimum at $\psi=0$ and another at $\psi=\psi_+$, where (for $b=g=1$):

$$\psi_+^2 = (1 + \sqrt{1 - 4r})/2. \quad (10)$$

The bulk phase transition takes place when the free-energy minima at $\psi=0$ and ψ_+ are equal, which occurs when the temperature $r=3/16 \equiv r_x$, in which case $\psi_+ = (3/4)^{1/2} \equiv \psi_x$. For $r > r_x$, the global minimum of $f_b(\psi)$ is at $\psi=0$, but the metastable minimum at ψ_+ persists up to a superheating spinodal temperature $r_* = 1/4$. In the range $r_x < r < r_*$, there is another positive value of ψ , denoted ψ_- , which satisfies $f_b(\psi_-) = f_b(\psi_+)$. This is given by

$$\psi_-^2 = (1 - 2\sqrt{1 - 4r})/2, \quad (11)$$

which approaches the isotropic value $\psi=0$ when $r \rightarrow r_x$.

III. SOLUTION OF THEORY

Due to the absence of a linear term in $f_s(\psi)$, Eq. (3), it can be shown that the theory outlined above always has a trivial solution $\psi(z)=0$ for all z [8], corresponding to an isotropic liquid state (denoted I) of the film with no smectic ordering whatsoever. According to any of the Eqs. (1), (4), or (9), the free energy $F \equiv F_I$ of this film state is zero, reflecting the fact that F only accounts for the effects of smectic ordering. In reality, such an isotropic free-standing film also exhibits a continuous density variation between vapor and liquid, and hence, has a positive free energy per unit area in excess of that in the complete absence of the film, approximately equal to $2\gamma_{v,l}$ where $\gamma_{v,l}$ is the (isotropic) liquid-vapor interfacial tension. This renders such a film metastable [22,23]. In addition, such an isotropic film should be unstable with respect to rupturing due to capillary-wave fluctuations [24]. It is presumed that smectic ordering diminishes the fluctuations which cause that instability.

In the overheated temperature regime $r > r_x$, nontrivial solutions for $\psi(z)$ exist provided the surface-enhancement field $g_s < 0$ (in practice, as shown later, for g_s less than some finite negative threshold). As in the closely related work of Ref. [15], for $r_x < r < r_*$, these solutions fall into two categories which can be distinguished by the values of the surface and midfilm order parameters ψ_s and ψ_0 : (a) $\psi_s > \psi_+$ and $\psi_0 \approx \psi_+$, representing a bulk-ordered state (denoted B) throughout the film; (b) $\psi_s > \psi_+$ but $\psi_0 \approx 0$, representing a surface-ordered state (denoted S) in which the interfaces are wet by the ordered phase while the middle of the film is practically disordered.

To determine the nontrivial solutions, we begin with Eq. (5), which clearly shows that such solutions are obtained only if $g_s < 0$. In practice, the solutions of Eq. (5) are found by squaring it, which leads [using f_b as given by Eq. (2)] to a cubic equation for the variable ψ_s^2 in terms of ψ_0 , whose roots are obtained analytically. The nature of those roots can be seen graphically, on plotting both sides of Eq. (5). A representative case is shown in Fig. 1, in the temperature range

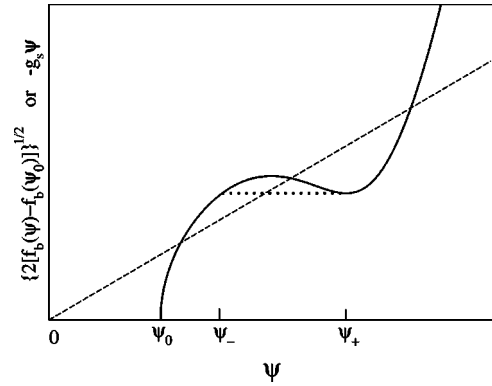


FIG. 1. Schematic graphical solution of Eq. (5) for $r_x < r < r_*$ and $0 < \psi_0 < \psi_-$. The solid curve is the function $\sqrt{2[f_b(\psi) - f_b(\psi_0)]}$ while the dashed straight line represents the function $-g_s\psi$ for a value of the parameter $g_s < 0$ which produces three roots of Eq. (5).

$r_x < r < r_*$ and for $0 < \psi_0 < \psi_-$. For the values of r and g_s considered in this case, the graph exhibits three roots for ψ_s . For the same r and for sufficiently larger (smaller) values of $|g_s|$, only the largest (smallest) root for ψ_s remains. However, it can be shown that the two smaller roots for ψ_s in Fig. 1 as well as the single small ψ_s root obtained for small values of $|g_s|$ correspond to unstable states. This is because those roots obey $\psi_s < \psi_+ \leq \psi_x = \sqrt{3/4}$, and hence, $\psi(z) \leq \psi_x$ for all z , giving positive values of the film free energy F (hence, unstable relative to the isotropic state) according to the argument following Eq. (9). When the temperature $r > r_*$, triple roots for the surface order parameter ψ_s can also occur for appropriate values of the surface coupling constant g_s and sufficiently small ψ_0 , but one can again show that only the largest of such roots produces a stable film state having $F < 0$.

Due to the integrals involving $[f_b(\psi) - f_b(\psi_0)]^{1/2}$ in Eqs. (4) and (6b), solutions with $\psi_- < \psi_0 < \psi_+$ and $\psi_s > \psi_+$ are forbidden. When $\psi_0 > \psi_+$, graphical constructions analogous to that in Fig. 1 show that there is only one mathematical root for ψ_s .

Having determined the unique root for ψ_s for a given midfilm order parameter ψ_0 , the solution of the theory is completed by solving Eqs. (6a) and (6b) to obtain ψ_0 for a given value of L . Under the conditions that, for all ψ_0 , the corresponding surface order parameter satisfies $\psi_s > \psi_+$, the function $G(\psi_0)$ has the typical behavior for $r_x < r < r_*$ shown by the solid curve in Fig. 2. It diverges logarithmically as $\psi_0 \rightarrow 0$, $\psi_0 \rightarrow \psi_-$ from below and $\psi_0 \rightarrow \psi_+$ from above [25], and, as mentioned earlier, is undefined for $\psi_- < \psi_0 < \psi_+$. For sufficiently small thickness L , Fig. 2 and Eq. (6a) indicate that the only nontrivial solution has $\psi_0 > \psi_+$, corresponding to a bulk-ordered state. This phase is stable with respect to the isotropic state if its free energy $F \equiv F_B$ satisfies $F_B < 0$. At larger values of L , greater than the minimum in $G(\psi_0)$ occurring for $0 < \psi_0 < \psi_-$, there are three possible nontrivial solutions for the mid-film order parameter ψ_0 . However, it can be shown that the intermediate solution (on the branch of $G(\psi_0)$ which diverges as $\psi_0 \rightarrow \psi_-$) always has a higher free energy F than both of the other two solutions. The solution with $\psi_0 > \psi_+$ describes, as before, a bulk-ordered phase, while that with $\psi_0 \approx 0$ corresponds to a surface-ordered

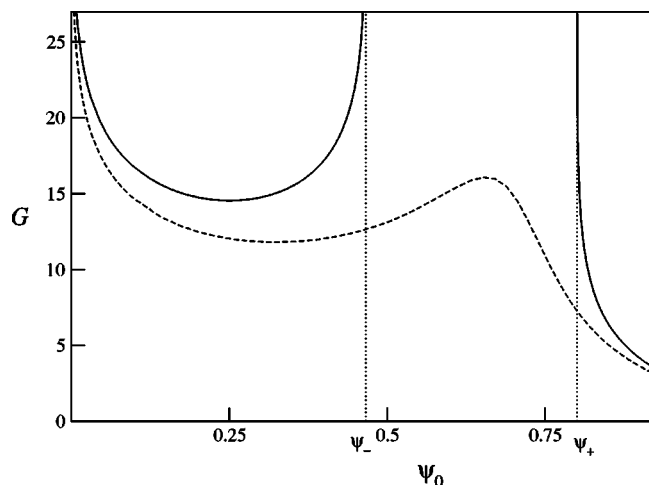


FIG. 2. The function $G(\psi_0)$ for $r_x < r < r_*$ (solid curve, $r=0.23$) and for $r_* < r < r_c$ (dashed curve, $r=0.26$). Here the surface coupling constant $g_s = -0.35$. The vertical dotted lines indicate the values of ψ_- and ψ_+ for the case $r=0.23$.

phase. The free energies of these phases must be compared with each other and with the isotropic phase $F_I=0$ to determine which phase is most stable. It follows from Eq. (7) that, since $f_b(\psi_+) > f_b(0)$ in the overheated regime, the free energy of the bulk-ordered state increases with thickness L more rapidly than that of the surface-ordered state, and hence, the latter is always more stable than the former at sufficiently large L . Physically, this just reflects the increasing bulk free-energy cost associated with the term $f_b(\psi_0)L \approx f_b(\psi_+)L$ in Eq. (4).

At temperatures r greater than the spinodal value r_* , the “forbidden” zone $\psi_- < \psi_0 < \psi_+$ vanishes. For a narrow range $r > r_*$, a remnant of the previous behavior remains, producing a finite maximum in $G(\psi_0)$ as shown by the dashed curve in Fig. 2. This persists up to some temperature denoted r_c . The value of r_c and height of the maximum in $G(\psi_0)$ are only weakly dependent on the values of the surface coupling constant g_s which yield this behavior. In this case, a first-order transition between bulk- and surface-ordered phases still occurs at a value of L between the minimum and maximum in $G(\psi_0)$. For $r > r_c$, the maximum in $G(\psi_0)$ disappears and this function decreases monotonically with increasing ψ_0 . In this case there is no distinction between bulk-ordered and surface-ordered phases. The film critical point at some temperature r_c has been noted in previous work [16,17].

We remark on some differences from the behavior of the liquid-crystal models studied in Refs. [16,17], which were based on a surface free energy $f_s(\psi) = g_s\psi^2/2 - h_s\psi$, with both $g_s, h_s \geq 0$. These models do not exhibit a completely isotropic state with $\psi(z)=0$ for all z . Rather, all film states have some degree of surface-induced ordering. The analog of the present isotropic to surface-ordered transition (the boundary-layer transition of Ref. [16]) is one in which the surface order parameter ψ_s undergoes a large jump between two nonzero values while the midfilm order parameter $\psi_0 \approx 0$ changes little. In Sheng’s model [16], which has $g_s=0$, this transition disappears when h_s becomes sufficiently large. In contrast, in the present model this transition persists for all values of $|g_s|$

greater than a minimal value 0.179 36, as discussed in the following subsection.

A. Asymptotic behavior: Surface-ordered phase

It turns out that many qualitative as well as quantitative features of the film phase behavior can be deduced from analytic studies of the asymptotic limit $L \rightarrow \infty$. In this limit, the two surfaces of the film are decoupled. First, considering the surface-ordered state in a thin film, we will show that it is closely related to the wetting of a single surface (here representing a liquid vapor interface) in a semi-infinite system [16–18]. This connection follows by considering the conditions for existence of the surface-ordered phase at arbitrarily large thickness L . Due to the logarithmic divergence of $G(\psi_0)$ as $\psi_0 \rightarrow 0$, the asymptotic solution of Eq. (6a) is [17]:

$$\psi_0 \approx e^{-\sqrt{r}L/2}. \quad (12)$$

On neglecting exponentially small terms, as well as using the fact that $f_b(\psi_0) \propto \psi_0^2$ for small ψ_0 , the term $f_b(\psi_0)L$ in the free energy F_S of the surface-ordered phase obtained from Eq. (4) can be neglected and that free energy becomes

$$F_S(L \rightarrow \infty) = 2f_s(\psi_s) + 2\sqrt{2} \int_0^{\psi_s} d\psi f_b^{1/2}(\psi) \equiv 2\gamma_{v,s}. \quad (13)$$

Here we have indicated that, in this limit, F_S is precisely twice the (smectic-ordering contribution to the) interfacial tension $\gamma_{v,s}$ between “vapor” and a semi-infinite surface-ordered isotropic liquid. Under the same approximation, i.e., setting $\psi_0=0$, Eq. (5) for ψ_s reduces to that for a semi-infinite isotropic liquid. The nontrivial solution of this equation for $\psi_s > \psi_+$ is

$$\psi_s = \psi_x \{1 + [1 + (g_s^2 - r)/r_x]\}^{1/2}. \quad (14)$$

Notice this requires that $g_s^2 > r - r_x$. Such a surface-ordered state in the semi-infinite system could still be metastable relative to the completely isotropic state (without any surface ordering). To check this we need the free energy from Eq. (13), which can be found analytically in the current model [28]:

$$\gamma_{v,s} = \frac{g_s}{2} \psi_s^2 + \frac{1}{4} \left[g_s(\psi_x^2 - \psi_s^2) + \sqrt{r} \psi_x^2 + \sqrt{3}(r - r_x) \ln \left(\frac{\psi_s^2 - \psi_x^2 - \sqrt{3}g_s}{\sqrt{3r - \psi_x^2}} \right) \right], \quad (15)$$

with surface order parameter ψ_s given by Eq. (14). In this asymptotic limit, the transition between isotropic and surface-ordered states occurs when $\gamma_{v,s}=0$. In the particular case of $r=r_x$, i.e., at the bulk transition temperature, the last two equations give (noting that $g_s < 0$):

$$\gamma_{v,s}(r=r_x) = \frac{3}{8}(g_s - 2g_s^2/\sqrt{3} + \sqrt{3}/8). \quad (16)$$

The negative root for g_s satisfying $\gamma_{v,s}(r=r_x)=0$ is $g_s = \sqrt{3}(1 - \sqrt{2})/4 = -0.179 36$. This is the minimal value of $|g_s|$ required to produce wetting by the ordered phase at the in-

terface of a semi-infinite isotropic liquid and for the existence of a surface-ordered phase in the limit $L \rightarrow \infty$ of a thin film. Larger values of $|g_s|$ are required to produce surface ordering at temperatures $r > r_x$. It should be noted that, in the present model, absent a linear term in $f_s(\psi)$, the ordered phase either completely wets the vapor-isotropic interface at bulk coexistence or is not adsorbed at all.

Since the deviations of the midfilm order parameter ψ_0 from 0 are exponentially small in L , the true phase boundary between isotropic and surface-ordered states in a finite-thickness film should show little dependence on thickness over a wide range of L , as noted in previous work [16,17]. Nonetheless, since $F_S(L)$ increases weakly with L for $\psi_0 > 0$ [see Eq. (7)], at finite values of L that phase boundary should occur at slightly higher values of r than predicted by the asymptotic estimate described earlier, increasingly so as L decreases.

B. Asymptotic behavior: Bulk-ordered phase

Next we examine the free energy of the bulk-ordered state for large thickness L and temperature $r < r_*$. Again, due to the logarithmic divergence of $G(\psi_0)$ as $\psi_0 \rightarrow \psi_+$, we find that $\psi_0 \rightarrow \psi_+ + O(e^{-a(r)L})$ where $a(r)$ is temperature dependent and positive. In the neglect of exponentially small terms, the free energy F_B of the bulk-ordered phase obtained from Eq. (4) separates into bulk and surface contributions given by

$$F_B(L \rightarrow \infty) = f_b(\psi_+)L + 2\gamma_{v,B}, \quad (17)$$

where

$$\gamma_{v,B} = f_s(\psi_s) + \sqrt{2} \int_{\psi_+}^{\psi_s} d\psi [f_b(\psi) - f_b(\psi_+)]^{1/2}. \quad (18)$$

Here the surface order parameter $\psi_s = \psi_s(\psi_+)$ is obtained from Eq. (5) with midfilm value $\psi_0 = \psi_+$. The quantity $\gamma_{v,B}$ can be interpreted as the (smectic-ordering contribution to the) interfacial tension between vapor and a semi-infinite bulk-ordered phase. Note that for $r > r_x$, the latter phase is metastable. The term $f_b(\psi_+)L$ in Eq. (17) gives the bulk free-energy cost of forming a film of thickness L from such a metastable phase. The integral in Eq. (18), like that for $\gamma_{v,S}$, can also be obtained analytically [28], with the result

$$\begin{aligned} \gamma_{v,B} = & \frac{g_s}{2} \psi_s^2 + \frac{\psi_s}{4\sqrt{3}} (\psi_s^2 - \psi_+^2 - 3/4) (\psi_s^2 + 2\psi_+^2 - 3/2)^{1/2} \\ & + \frac{3}{16} \psi_+ (\psi_+^2 - 1/2) - \frac{\sqrt{3}}{2} (\psi_+^2 - 3/4) (\psi_+^2 - 1/4) \\ & \times \ln \left[\frac{\psi_s + (\psi_s^2 + 2\psi_+^2 - 3/2)^{1/2}}{\psi_+ + \sqrt{3}(\psi_+^2 - 1/2)^{1/2}} \right]. \end{aligned} \quad (19)$$

Equating the asymptotic expressions Eqs. (13) and (17), an approximate relation for the boundary between the surface-ordered and bulk-ordered phases is

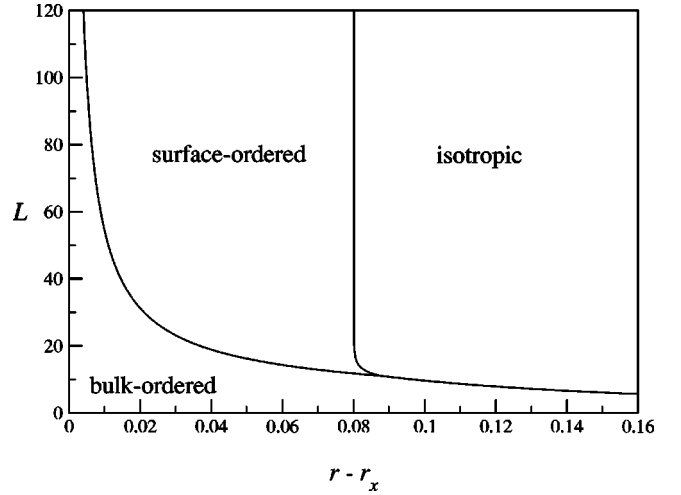


FIG. 3. Phase diagram for $g_s = -0.35$. The solid lines are the equilibrium phase boundaries between the indicated phases.

$$L_{S-B} \approx \frac{2(\gamma_{v,S} - \gamma_{v,B})}{f_b(\psi_+)}. \quad (20)$$

The corresponding asymptotic equation for the boundary between isotropic and bulk-ordered phases is

$$L_{I-B} \approx -\frac{2\gamma_{v,B}}{f_b(\psi_+)}. \quad (21)$$

The last two equations will be compared with the numerically-determined solutions in the next section.

IV. RESULTS

The main results of this work are film phase diagrams and their properties in terms of the thickness L and temperature r . A representative phase diagram is shown in Fig. 3, for the value of the surface coupling constant $g_s = -0.35$. This exhibits isotropic, bulk-ordered and surface-ordered phases, separated by first-order phase boundaries (solid lines) which meet at a triple point. Except very close to the triple point, the boundary between the isotropic and surface-ordered phases is essentially independent of L , as noted at the end of Sec. III A. For this value of g_s , the critical point between bulk-ordered and surface-ordered phases mentioned in Sec. III is not observed, as it is preempted by transitions from both phases to the isotropic phase. That type of critical point is found at values of $|g_s|$ slightly larger than 0.35 [27], but the resulting phase diagrams do not match any observed in connection with layer-thinning, and hence, are not examined here. Phase diagrams obtained at smaller values of $|g_s|$ are qualitatively similar to that in Fig. 3, differing in that the triple point moves to smaller r and larger L , and eventually disappears as $|g_s|$ approaches the value 0.17936. For smaller values of $|g_s|$ than this, only the bulk-ordered and isotropic phases occur [15].

We find that Eqs. (20) and (21), with the interfacial tensions given by Eqs. (15) and (19), accurately describe their respective transition lines in the temperature range $r_x < r < r_*$. (Note that $\gamma_{v,B}$ and ψ_+ are undefined for $r > r_*$.)

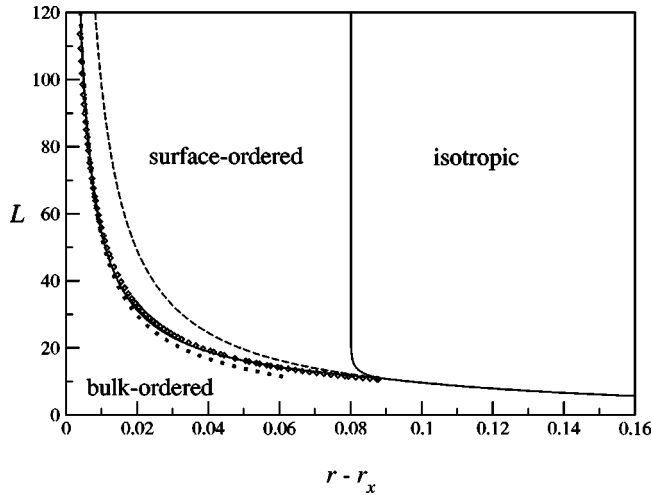


FIG. 4. Same as Fig. 3, but now showing the metastable phase boundary (dashed curve) between isotropic and bulk-ordered phases at values of r below the triple point, which is accurately fit by the Kelvin law $L \approx (\Delta r)^{-1.0}$ over its whole range. The best-fit power law to the transition line between bulk-ordered and surface-ordered phases [$L \approx (\Delta r)^{-0.76}$] is indicated by the open squares, while the dotted curve is the asymptotic approximation to this transition line given by Eq. (23), which terminates at the superheating spinodal temperature $r = r_*$.

The phase boundaries of Fig. 3 are reproduced in Fig. 4, where the (numerically determined) continuation of the transition line between isotropic and bulk-ordered phases at temperatures below the triple point is shown by the dashed curve. Note that along this line both phases are metastable relative to the surface-ordered phase. The results of Eqs. (20) and (21) are essentially indistinguishable from those in Fig. 4 in the temperature range $r_x < r < r_*$. The error in Eq. (20) at $r = r_*$ is about 1.5% while that in Eq. (21) is only about 0.06%. As r approaches the bulk transition temperature r_x , $\psi_+ \rightarrow \psi_x$ and $f_b(\psi_+) \rightarrow \psi_x^2 \Delta r / 2$ where $\Delta r = r - r_x$. In this limit, on approximating $\gamma_{v,S}$ and $\gamma_{v,B}$ by their values at the bulk transition temperature, Eqs. (20) and (21) both yield the “Kelvin law” [4,17,18] $L \approx (\Delta r)^{-1}$. This asymptotic law very well fits the isotropic to bulk-ordered transition for all r . A best fit with a single power-law to the curve for L_{I-B} in Fig. 4, including both sides of the triple point, gives $L_{I-B} = 0.936(\Delta r)^{-1.011}$, virtually indistinguishable from that curve. The main reason for this agreement over a wide range is cancellation between negative deviations from the asymptotic relation $f_b(\psi_+) \approx \psi_x^2 \Delta r / 2$ and negative deviations of $|\gamma_{v,B}|$ from its value at the bulk transition.

On the other hand, we find that the transition line between bulk-ordered and surface-ordered phases deviates significantly from the asymptotic Kelvin relation $L_{S-B} \propto (\Delta r)^{-1}$. The best-fit power law to the exact curve for L_{S-B} in Fig. 4 over the displayed range of thickness (i.e., $L < 120$) and below the triple-point temperature, shown by the square symbols, is $L_{S-B} = 1.67(\Delta r)^{-\nu}$, where $\nu = 0.761$. When the fitting is extended to include the $I-B$ curve above the triple point, the exponent changes to $\nu = 0.781$. These values of ν are close to the range observed for layer-thinning transitions [1–3,11]. Of course, the values of the exponent ν in these fits increase if

the fitting is done over a larger range of L values. Extending the fit of L_{S-B} to values $L \approx 1000$ yields decay exponents around $\nu = 0.80$. We will discuss in Sec. V why it is plausible to limit the fits of L_{S-B} to the smaller range of thickness L shown in Figs. 3 and 4.

Scaling corrections to the Kelvin law are expected, among other reasons, due to the growth of a complete-wetting layer of the bulk ordered (smectic- A) phase at the vapor-isotropic interface as $r \rightarrow r_x$ [17,18]. In this limit

$$(\gamma_{v,S})_x - (\gamma_{v,B})_x = (\gamma_{I,B})_x, \quad (22)$$

where the subscript x denotes bulk coexistence and $\gamma_{I,B} > 0$ is the interfacial tension between semi-infinite isotropic and bulk-ordered phases. Since the latter is independent of the surface coupling constant g_s , the asymptotic relation Eq. (20) becomes independent of g_s as $\Delta r \rightarrow 0$, confirmed by numerical calculations. Following arguments by Evans *et al.* [18], on using a leading-order expansion of $\gamma_{v,S}$ about its value at the bulk transition, Eqs. (20) and (22) give

$$L_{S-B} \approx 2l + \frac{2(\gamma_{I,B})_x}{f_b(\psi_+)}, \quad (23)$$

where l is the thickness of the ordered wetting layer at the vapor-isotropic interface, which diverges proportional to $|\ln(\Delta r)|$ as $\Delta r \rightarrow 0$. This can be evaluated analytically in the present model, for example, from the distance between the wall and the inflection point in the $\psi(z)$ profile [28]. Nonetheless, as shown by the dotted curve in Fig. 4, Eq. (23) does not fully account for the observed scaling corrections to the Kelvin law for the surface-ordered to bulk-ordered transition, especially on approaching the bulk spinodal temperature r_* , where the assumptions underlying the asymptotic expansion break down.

V. CONCLUDING REMARKS

The principal finding of this paper is the fact that the transition between surface-ordered and bulk-ordered phases is closely fit by an effective power-law relation $L \propto (\Delta r)^{-\nu}$ with ν as small as 0.76. Since the scaling law should asymptotically approach the Kelvin relation $L \propto (\Delta r)^{-1}$, the value of the exponent ν increases with increase in the range of L values considered. However, it is plausible to truncate the fits at the smaller range of L shown in Figs. 3 and 4. As mentioned in Ref. [21], in this paper all distances are expressed in units of the “zero-temperature” correlation length ξ . The relation between ξ and the molecular length, and hence, smectic layer spacing is uncertain: there have been (to our knowledge: see also Ref. [29]) no fittings of Landau–de Gennes theory to experiment for the properties of the isotropic-smectic transition analogous to those done for isotropic-nematic transitions [16,30]. In the latter cases, it is typically found that the zero-temperature correlation length ξ is a fraction—between 1/3 and 1/2—of the molecular length [16,30]. If this also holds for the isotropic-smectic transition, then $L \approx 120$ corresponds to a thickness of 40–60 smectic layers, at the high end of experimental studies [1–3,11] of free-standing films with first-order layer-thinning transitions.

We have presented results for the particular value of the surface coupling constant $|g_s|=0.35$, which we believe is at the upper end of realistic values of this parameter. For smaller values of $|g_s|$, the *I-S-B* triple point moves to larger thickness L and smaller temperature difference Δr , which also results in larger values of the effective exponent ν . For example, using $g_s=-0.30$, we find ν to be in the range 0.77–0.87, depending on the L range which is fitted. All these results point to the fact that there is no unique value for the layer-thinning exponent ν , which is consistent with experimental observations [1–3,9,11].

In this study, we have treated the film thickness L as a continuous variable. When strain effects are included, as in earlier work based on de Gennes' original model for a presmectic film [7–11], the film free energy of both the bulk-ordered and surface-ordered phases is expected to exhibit a series of wells with minima at approximately integer multiples of the smectic layer spacing. The phase boundaries between these “quantized” states and with the isotropic phase should lie very close to the continuous phase boundaries displayed in Fig. 3.

As in other work [4,5], true layer-thinning transitions do not necessarily coincide with the equilibrium transitions between bulk-ordered and surface-ordered (or isotropic) states at a given thickness L , which can also modify the observed values of the effective exponent ν . Mirantsev [4] has argued that, following a transition from an N -layer bulk-like state to the surface-ordered or quasi-smectic state, the film thins down to an $(N-n)$ -layer state ($n \geq 1$) of lower free energy. While plausible, this intermediate role of the quasismectic state is unlikely in view of studies [11,12] showing that layer

thinning occurs by nucleation and growth of dislocation loops between the N - and $(N-n)$ -layer regions. Nonetheless, the generic nature of the surface-ordered phase found in the present and other models [4,5,15–17] under conditions of sufficiently strong surface enhancement suggests that its *potential* (if not actual) presence could be a necessary condition for the occurrence of layer-thinning transitions. A complete investigation of layer thinning is expected to require analysis of the competing kinetic pathways available to the system near the “equilibrium” transitions studied here, as done in previous work [9–11] based on the original second-order presmectic model of de Gennes [14].

Finally, we call attention to the dependence of the bulk-ordered free energy on thickness L , as shown by Eqs. (4) and, asymptotically, Eq. (17). In the latter limiting case, the term linear in L exists due to the metastability of the bulk-ordered phase, depends only on the degree of overheating (as postulated in Ref. [11]), and has no connection to the meniscus effects invoked in other work on layer-thinning based on de Gennes' presmectic model in the case of systems undergoing *second-order* smectic-nematic transitions [9,13]. Due to the significant nonzero values of ψ_+ , Eq. (17) has a stronger dependence on L than the free energy of systems undergoing second-order transitions, and hence, should be sufficient (in the absence of meniscus effects) to provide the major “driving force” in dislocation-nucleation mechanisms of layer-thinning transitions.

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- [1] T. Stoebe, P. Mach, and C. C. Huang, *Phys. Rev. Lett.* **73**, 1384 (1994).
- [2] P. M. Johnson, P. Mach, E. D. Wedell, L. Lintgen, M. Neubert, and C. C. Huang, *Phys. Rev. E* **55**, 4386 (1997).
- [3] S. Pankratz, P. M. Johnson, H. T. Nguyen, and C. C. Huang, *Phys. Rev. E* **58**, R2721 (1998).
- [4] L. V. Mirantsev, *Phys. Lett. A* **205**, 412 (1995); *Liq. Cryst.* **20**, 417 (1996).
- [5] Y. Martinez-Raton, A. M. Somoza, L. Mederos, and D. E. Sullivan, *Faraday Discuss.* **104**, 111 (1996); *Phys. Rev. E* **55**, 2030 (1997).
- [6] T. Kranjc and S. Zumer, *J. Chem. Phys.* **105**, 5242 (1996).
- [7] E. E. Gorodetskii, E. S. Pikina, and V. E. Podnek, *JETP* **88**, 35 (1999).
- [8] A. N. Shalaginov and D. E. Sullivan, *Phys. Rev. E* **63**, 031704 (2001).
- [9] F. Picano, P. Oswald, and E. Kats, *Phys. Rev. E* **63**, 021705 (2001).
- [10] A. N. Shalaginov and D. E. Sullivan, *Phys. Rev. E* **65**, 031715 (2002).
- [11] S. Pankratz, P. M. Johnson, R. Holyst, and C. C. Huang, *Phys. Rev. E* **60**, R2456 (1999).
- [12] S. Pankratz, P. M. Johnson, A. Paulson, and C. C. Huang, *Phys. Rev. E* **61**, 6689 (2000).
- [13] A. Poniewierski, P. Oswald, and R. Holyst, *Langmuir* **18**, 1511 (2002).
- [14] P. G. deGennes, *Langmuir* **6**, 1448 (1990).
- [15] A. Weinstein and S. A. Safran, *Europhys. Lett.* **42**, 61 (1998).
- [16] P. Sheng, *Phys. Rev. A* **26**, 1610 (1982).
- [17] A. Poniewierski and T. J. Sluckin, *Liq. Cryst.* **2**, 281 (1987).
- [18] R. Evans, U. Marini Bettolo Marconi, and P. Tarazona, *J. Chem. Phys.* **84**, 2376 (1986).
- [19] P. G. deGennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993), p. 508.
- [20] H. Nakanishi and M. E. Fisher, *J. Chem. Phys.* **78**, 3279 (1983).
- [21] In particular, the normal distance z through the film is taken to be in units of $\sqrt{gC/b} \equiv \xi$, which can be considered a “zero-temperature” correlation length.
- [22] K. T. Chambers and C. J. Radke, in *Interfacial Phenomena in Petroleum Recovery*, edited by N. R. Morrow (Dekker, New York, 1991), p. 191.
- [23] Y. Martinez, A. M. Somoza, L. Mederos, and D. E. Sullivan, *Phys. Rev. E* **53**, 2466 (1996).
- [24] D. Bhatt, J. Newman and C. J. Radke, *J. Phys. Chem. B* **106**, 6529 (2002).
- [25] The integral $G(\psi_0)$ was evaluated numerically, first transforming to the integration variable $x=(\psi^2-\psi_0^2)^{1/2}$ to remove the

apparent singularity at $\psi \rightarrow \psi_0$. The logarithmically divergent contributions at $\psi_0 \rightarrow 0$, ψ_- and ψ_+ were extracted analytically and the residual integrals were evaluated by an adaptive Romberg extrapolation technique [20,26].

- [26] W. H. Press *et al.*, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986), Chap. 4.
[27] The triple point in Fig. 3 occurs at a value $r=0.275\ 37$, which

lies between the spinodal temperature $r_s=1/4$ and the critical temperature $r_c \approx 0.30$ for this case.

- [28] R. Lipowski and W. Speth, *Phys. Rev. B* **28**, 3983 (1983).
[29] P. K. Mukherjee, H. Pleiner, and H. R. Brand, *Eur. Phys. J. E* **4**, 293 (2001).
[30] *Introduction to Liquid Crystals*, edited by E. B. Priestly, P. J. Wojtowicz, and P. Sheng (Plenum, New York, 1975), Chap. 10.