Landau−de Gennes theory of surface-enhanced ordering in smectic films

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A Landau theory for surface-enhanced ordering in smectic-*A* free-standing films is described, based on a generalization of de Gennes' model for a ''presmectic'' fluid confined between two walls. According to the theory, smectic ordering in free-standing films heated above the bulk smectic melting temperature is due to an intrinsic surface contribution rather than an external field. The theory yields a persistent finite-size effect, in that the film melting temperatures do not tend to the bulk transition temperature in the limit of infinite film thickness. It also predicts that a continuous transition from $(N+1)$- to N-layer films is impossible without an external field. The theory closely fits existing experimental data on layer-thinning transitions in compounds which exhibit a bulk smectic-*A* to nematic phase transition. Possible origins of the intrinsic surface contribution are discussed.

I. INTRODUCTION

Several years ago Stoebe *et al.* [1] discovered that free-standing smectic-*A* (Sm*A*) films of certain fluorinated liquid-crystalline compounds could remain stable on being heated to temperatures above that of the bulk Sm*A*-isotropic (*I*) phase transition. Instead of rupturing at the bulk transition temperature, as do free-standing films of most Sm*A* materials, the films studied in Ref. [1] were found to undergo a reproducible series of layer-thinning transitions at higher temperatures. At each transition, a film would spontaneously decrease in thickness by one or more smectic layers. Subsequently, layer-thinning transitions have been observed in a small number of other compounds which exhibit either Sm*A*-*I* transitions [2–4] or Sm*A*-nematic (*N*) transitions [5,6]. The relation between the film thickness in number of layers N and the layer-thinning transition temperatures $T_c(N)$ has been found to be well fitted by a simple power law, $N \propto t^{-\nu}$, where $t = [T_c(N) - T_0]/T_0$, with T_0 approximately equal to the bulk transition temperature. However, the fitting exponent ν is found to lie in a rather wide range, $0.61 \leq \nu \leq 0.82$.

Several mean-field theories have attempted to explain layer-thinning behavior [7–11]. As was suggested by Stoebe *et al.* [1], these theories attribute the stability of a free-standing smectic film above the bulk disordering temperature to enhanced smectic ordering associated with the free surfaces of the film, although the theories differ in the details by which this enhanced ordering arises. In most of these theories, it is envisioned that the thinning of an *N*-layer film proceeds by melting of the interior layers into either a nematic [9] or a so-called ''quasismectic'' state [7,10], after which the excess fluid is squeezed out and the film is reconstituted with a smaller number of layers. A different picture was postulated in Ref. [11], according to which thinning occurs prior to the vanishing of the Sm*A* order in the film interior, on reaching certain critical points where the balance between external compressive forces and film elastic forces is lost. However, none of the theories has been able to account for properties such as the values of the exponent ν in the power-law relation or the relative scarcity of suitable materials which exhibit layer thinning.

Recent visual observations and optical reflectivity studies by Pankrantz *et al.* [12,13] of layer-thinning transitions in compounds which undergo first-order Sm*A*-*I* transitions reveal that thinning in these cases occurs by spontaneous nucleation of dislocation loops, the growth of which causes a film to thin. A model of this process was described in Ref. [12], predicting a $T_c(N)$ dependence which is functionally different from the power-law relation but which also fits experimental data closely.

In this paper we develop a mean-field theory for layer thinning in compounds that exhibit *second-order* bulk phase transitions. While, in principle, this restricts the application of the theory to those systems exhibiting bulk Sm*A*-*N* rather than first-order Sm*A*-*I* transitions, we justify this treatment by the greater simplicity of its analysis and by the fact that the observed layer-thinning behavior in both types of systems is similar [1–6]. The theory is a modification of an earlier Landau theory described by de Gennes [14] for a ''presmectic'' fluid confined between two parallel solid walls [15]. The latter theory was also considered in Ref. [11], and some aspects of it were utilized in the model described in Ref. [12]. In de Gennes' original theory, surface-enhanced Sm*A* order is induced by an external-field-like coupling term in the Landau free energy, which is *linear* in the surface smectic order parameter. Here, we modify that theory by including a *quadratic* term in the surface smectic order parameter while neglecting the external-field term. We will argue later that this model is more appropriate for free-standing films. The original de Gennes theory is also extended to include nonharmonic terms in the bulk free-energy density, which is necessary to prevent divergences occurring close to the bulk transition temperature in earlier studies based on this theory [11,12,14]. We derive a simple analytic formula for the variation of $T_c(N)$ with N which fits experimental data very closely. This result demonstrates that the power-law relation deduced experimentally is only an approximate ''fit'' and that there is no universal value of the exponent ν. We also find one difference from previous interpretations of layer thinning, namely that the layer-thinning transition temperatures $T_c(N)$ approach a limiting tempera-

ture for large N which lies slightly *above* the bulk mean-field transition temperature. Nonetheless, this difference is compatible with experimental measurements in the case of systems with bulk SmA-N transitions [5,6].

We also examine the conditions required for the existence of a continuous transition from N to $(N\pm1)$ layers *without* nucleation of dislocation loops, which was predicted by de Gennes to occur according to his original model [14] for a ''presmectic'' fluid between two walls. By examining the maximal possible changes in thickness due to deformations of the smectic layers, it will be shown that the presence of an external field is necessary for such a continuous transition, and therefore that the latter does not occur in the present model. In place of that transition, we surmise that either film rupturing *or* growth of dislocation loops must occur.

This paper is organized as follows. In Sec. II we introduce the generalized ''presmectic'' model for the the free energy of a film and derive the corresponding Euler-Lagrange equations and supplementary boundary conditions. We present an analysis of solutions to the equations and calculate the equilibrium free energy. In Sec. III we use the analysis to find the maximal temperature $T_c(N)$ at which an N-layer film is stable, showing that the model agrees with experimental data on layer thinning. Section IV examines whether the present model allows for a continuous transition from N to $(N\pm1)$ layers on varying the film thickness. In Sec. V we summarize the results as well as discuss possible mechanisms for the origin of the intrinsic surface contribution to the free energy.

II. SMECTIC ORDER PARAMETER AND FREE ENERGY

Following Refs. [11,14], we model a free-standing smectic film by a thin film of liquid bounded by two parallel surfaces located at $z=\pm L/2$, where L is the film thickness. The local smectic order in the film is represented by the complex order parameter Ψ [16,17] whose real part characterizes the spatial modulation of the density, given by

$$\Psi=\psi\exp[\iota q_0(z-u)+\iota\phi_0], \qquad (1)$$

where ψ is the real amplitude, u is the layer displacement field, q_0 equals $2\pi/d$ with d being the unstressed layer spacing, and ϕ_0 is an initial phase which we will choose to guarantee that the film surfaces occur at minima of $\mathrm{Re}\,\Psi$. We associate the maxima of $\mathrm{Re}\,\Psi$ with the midpoints of the smectic layers. In general, ψ and u are functions of three spatial coordinates (x,y,z), but here we assume the system to be uniform in the (x,y) plane and consider only a dependence on distance z normal to the film. We take the Landau free energy, per unit area, for the system to be

$$F=\frac{1}{2}\int_{-L/2}^{L/2}dz\left[r\psi^2+\frac{1}{2}g\psi^4+C(\nabla_z\psi)^2+Cq_0^2\psi^2(\nabla_z u)^2\right]$$
$$+\frac{1}{2}r_s[\psi^2(L/2)+\psi^2(-L/2)]-h_s[\psi(L/2)+\psi(-L/2)],$$
$$(2)$$

where C is an elastic constant. This free energy generalizes that used in [14] by including both a quartic term $(g/4)\psi^4$ in the bulk free-energy density and quadratic terms $r_s\psi^2$ $(\pm L/2)/2$ in the contribution of the surface layers to the free energy. Along with the terms $-h_s\psi(\pm L/2)$, where h_s could be considered an external anchoring field, the form of the surface contributions in Eq. (2) are analogous to those introduced a while ago in Landau theories of wetting and criticality in semi-infinite systems and thin films [18]. A similar Landau model, neglecting linear terms analogous to those with h_s but including additional nonlinear terms in the surface order parameters $\psi(\pm L/2)$, was recently applied to surface-induced freezing [19].

The bulk free-energy density $(r/2)\psi^2+(g/4)\psi^4$ in Eq. (2), with $g>0$, is appropriate for a *second-order* bulk phase transition, which occurs at $r=0$ in this mean-field model. In this work we will only consider overheated films with $r\geq0$, expressing $r=a(T-T^*)$, where T^* denotes the bulk mean-field transition temperature [17]. Besides the correlation length $\xi=\sqrt{C/r}$ [16,17] in the bulk isotropic phase, there is an additional characteristic length $\xi_s=C/|r_s|$ associated with the surfaces. By appropriate scaling (e.g., $z/d\rightarrow z$, ψ/d^3 $\rightarrow\psi$, $rd^2/C\rightarrow r$, $Fd/C\rightarrow F$, etc.), one can regard all parameters and variables in Eq. (2) as dimensionless as well as set $C=1$, although for clarity we will keep $C\neq1$ in the following analysis, other than in numerical calculations.

Note that, in the absence of any smectic ordering [i.e., $\psi(z)=0$ for all z], the free energy F defined in Eq. (2) is zero. This circumstance does not necessarily correspond to the absence of a free-standing film, since the latter would still be characterized by a nontrivial density profile and associated film tension. However, such a *structureless* free-standing film has never been observed and, presumably, is completely unstable with respect to fluctuations which lead to film rupturing [8].

A. Euler-Lagrange equations

The Euler-Lagrange equations for ψ and u obtained by minimizing Eq. (2) are

$$C\nabla_z^2\psi=[r+Cq_0^2(\nabla_z u)^2]\psi+g\psi^3, \qquad (3a)$$

$$\nabla_z(\psi^2\nabla_z u)=0, \qquad (3b)$$

with accompanying boundary conditions

$$\pm C\nabla_z\psi(z=\pm L/2)=h_s-r_s\psi(z=\pm L/2), \qquad (4a)$$

$$q_0[L-2u(L/2)]=2\pi N, \qquad (4b)$$

where N is the number of layers. The first boundary condition Eq. (4a) is obtained from variation of the free energy, while the second condition Eq. (4b) follows on assuming that the phase of the order parameter at the surfaces is fixed in order to guarantee that there is an integer number of layers in the range of z between $-L/2$ to $L/2$. We have used the fact that the film is symmetrical about its midpoint at $z=0$, and hence that $\psi(z)=\psi(-z)$, $u(z)=-u(-z)$ and, as a consequence, $u(0)=0$. Note that the second boundary condition is

the same as that used by de Gennes [14] for a ''presmectic'' liquid confined between two walls, where it implies that the smectic layers at both film surfaces stick exactly to the walls. The same condition was also used for a free-standing smectic film in [11], while the latter work used undetermined values for $\psi(\pm L/2)$.

The solution to the second Euler-Lagrange equation Eq. (3b) can be expressed as

$$u(z) = A \int_0^z dz' \, \psi^{-2}(z'), \tag{5}$$

where we used $u(0) = 0$. In view of Eq. (4b), the coefficient A has to satisfy

$$Nd = L - 2A \int_0^{L/2} dz' \, \psi^{-2}(z'). \tag{6}$$

Integrating Eq. (3a) once yields

$$C(\nabla_z \psi)^2 = r\psi^2 + \frac{1}{2} g\psi^4 - A^2 C q_0^2 \psi^{-2} + B, \tag{7}$$

where the constant B is chosen to satisfy the condition $\nabla_z \psi(0) = 0$ (which follows from symmetry) and hence is given by

$$B = -r\psi^2(0) - \tfrac{1}{2} g\psi^4(0) + A^2 C q_0^2 \psi^{-2}(0). \tag{8}$$

Since the right-hand side of Eq. (7) must be positive, and (for $r > 0$, $g > 0$) is a monotonically increasing function of ψ, it is necessary that $\psi(z) \geq \psi(0)$ for all z. This in turn dictates the sign of $\nabla_z \psi$ and hence the form of the first boundary condition Eq. (4a),

$$\sqrt{C}\left[r\psi^2(L/2) + \frac{1}{2} g\psi^4(L/2) - A^2 C q_0^2 \psi^{-2}(L/2) + B \right]^{1/2}$$
$$= h_s - r_s \psi(L/2). \tag{9}$$

The latter equation determines the value of the order parameter $\psi(L/2)$ at the surface for given values of A and $\psi(0)$. If a set of values of A, $\psi(0)$, and $\psi(L/2)$ is known, then $\psi(z)$ can be found as the inverse function to

$$z = \sqrt{C} \int_{\psi(0)}^{\psi(z)} d\psi \left[r\psi^2 + \frac{1}{2} g\psi^4 - A^2 C q_0^2 \psi^{-2} + B \right]^{-1/2}, \tag{10}$$

which follows from Eq. (7). Setting $z = L/2$ in Eq. (10) provides an equation which together with Eqs. (6) and (9) allows one to determine the unknown quantities A, $\psi(0)$, and $\psi(L/2)$. That equation can be written as

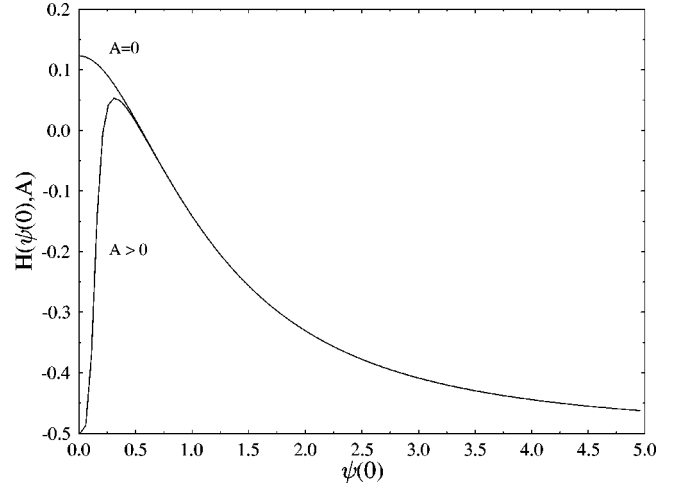$$H(\psi(0), A) = 0, \tag{11}$$

where we have defined the function

FIG. 1. The function $H(\psi(0), A)$ for $r_s = -0.2$, $r = 0.08$, $g = 0.04$, $h_s = 0$, $L/d = 5$, and $C = 1$.

$$H(\psi(0), A) = \frac{\sqrt{C}}{L} \int_{\psi(0)}^{\psi(L/2)} d\psi \left[r\psi^2 + \frac{1}{2} g\psi^4 \right.$$
$$\left. - A^2 C q_0^2 \psi^{-2} + B \right]^{-1/2} - \frac{1}{2}, \tag{12}$$

and where $\psi(L/2)$ is determined from Eq. (9).

The routine we have used for obtaining solutions to the equations above is the following. First we scan over values of A. For each trial value of A, we vary $\psi(0)$. For each value of $\psi(0)$, we determine all the real, positive solutions for $\psi(L/2)$ from the roots of Eq. (9). Although there may be multiple roots of that equation, only one of them (if any), when used as $\psi(L/2)$ in Eq. (11), can satisfy the latter equation for any given value of L. We then find that pair of values of $\psi(0)$ and $\psi(L/2)$ which satisfies Eq. (11). There can be none, one or two such pairs. This is indicated by Fig. 1, which shows typical curves of the function $H(\psi(0), A)$ vs $\psi(0)$ for $h_s = 0$ and $r > r_s^2/C$, where the significance of the latter conditions will be described in Sec. III. If $|A|$ is sufficiently large, then $H(\psi(0), A)$ is negative in the whole range of $\psi(0)$ and there is no solution pair. For some range of $|A|$, the maximum of $H(\psi(0), A)$ as a function of $\psi(0)$ is positive. There are two pairs of $\psi(0)$ and $\psi(L/2)$ in this case. Both pairs correspond to physical solutions for different thicknesses L of the film. If $A = 0$ then the function $H(\psi(0), A)$ decays monotonically with increasing $\psi(0)$. In this case, there can be none or one solution pair (the point of disappearance of a pair is considered in detail in Sec. III). Finally, in scanning over A, we find that value of A which satisfies Eq. (6). The integrand of Eq. (10) has an integrable singularity at the lower limit proportional to $[\psi - \psi(0)]^{-1/2}$. This term was subtracted out and integrated analytically. The integration of the residual integral in Eq. (10) as well as that in Eq. (6) were performed by Simpson's method.

B. Equilibrium free energy

Once a solution to the Euler-Lagrange equations and boundary conditions is known, the equilibrium free energy

can be determined from Eq. (2). Using integration by parts and rearranging the term $g\psi^4$, the latter equation can be re-written as

$$F = \frac{1}{2}\int_{-L/2}^{L/2} dz[r\psi + g\psi^3 - C\psi\nabla_z^2 + Cq_0^2\psi(\nabla_z u)^2]\psi$$

$$- \frac{1}{4}\int_{-L/2}^{L/2} dz\, g\psi^4 + \frac{1}{2}C[\psi(L/2)\nabla_z\psi(L/2)$$

$$- \psi(-L/2)\nabla_z\psi(-L/2)] + \frac{1}{2}r_s[\psi^2(L/2)$$

$$+ \psi^2(-L/2)] - h_s[\psi(L/2) + \psi(-L/2)]. \quad (13)$$

At equilibrium, the integral term in the first line is equal to zero due to Eq. (3a). The nonintegral terms involving r_s cancel each other because of the boundary conditions Eq. (4a). Using symmetry, the last equation then gives for the equilibrium free energy, denoted F_{eq},

$$F_{eq} = -\frac{1}{2}g\int_0^{L/2} dz\,\psi^4(z) - h_s\psi(L/2). \quad (14)$$

This expression is significant for showing that the equilibrium free energy in the presence of smectic ordering is necessarily negative for positive fields h_s and g.

The equilibrium free energy can also be expressed through the work done by the external field h_s. To find that, consider the variation of the free energy due to variations in h_s,

$$\delta F = -\delta h_s[\psi(L/2) + \psi(-L/2)], \quad (15)$$

where contributions resulting from any variations $\delta\Psi(z)$ about its equilibrium solution are zero. Integrating Eq. (15) yields

$$F_{eq} = F_{eq}(h_s=0) - \int_0^{h_s} dh[\psi(L/2,h) + \psi(-L/2,h)], \quad (16)$$

where $\psi(z,h)$ is the solution to the Euler-Lagrange equations for a given surface field h. The second term in Eq.(16) is the work done by the external field. Equation (16) generalizes an expression given by de Gennes [14]. Note that if $r_s=0$ and $g=0$, then the smectic order in an overheated film is solely due to the external field and $\psi(L/2,h_s)\propto h_s$, as can be shown from Eqs. (6), (9), and (10). In this case Eq. (16) gives $F_{eq} = -h_s\psi(L/2)$, in agreement with Eq.(14).

III. FILM CRITICAL LINE

In this section we consider an overheated smectic film with external field $h_s=0$ but nonzero surface coupling constant r_s. We believe that these model conditions apply to free-standing films, due to the fact that the Euler-Lagrange equations (3a), (3b) and boundary conditions (4a) in this case always admit a trivial solution $\psi(z)=0$, corresponding to the absence of any smectic ordering. Nontrivial solutions exhib-

iting smectic order can occur, induced by the r_s surface terms in the free energy for sufficiently small $r\propto T-T^*$, provided $r_s<0$ [see Eq. (9)] [20]. At higher temperature, the bulk contributions to the free energy become dominant and smectic ordering disappears. For a fixed value of r_s, we will show that there is a ''critical'' line in the (L,T) plane at which stable nontrivial solutions for ψ and u develop. To find this line, we examine the solutions of the simultaneous equations (9) and (11). As seen in Fig. 1, the largest value of $H(\psi(0),A)$ occurs when $A=0$ and $\psi(0)=0$, while H tends to the value $-1/2$ as $\psi(0)\rightarrow\infty$. A nontrivial solution for $\psi(0)$ exists only if $H(0,0)\geq 0$, and the critical locus corresponds to the condition $H(0,0)=0$.

To find the limit $\psi(0)\rightarrow 0$ of $H(\psi(0),0)$, we express Eq. (12) in terms of the variable $\chi\equiv\psi/\psi(0)$,

$$H(\psi(0),0) = \frac{\sqrt{C}}{L}\int_1^{\chi_{max}} \frac{d\chi}{\sqrt{r(\chi^2-1)+\frac{1}{2}g\psi^2(0)(\chi^4-1)}}$$

$$-\frac{1}{2}, \quad (17)$$

where $\chi_{max}\equiv\psi(L/2)/\psi(0)$. Setting $\psi(0)=0$, the integral can be evaluated analytically to give

$$H(0,0) = \frac{1}{L}\sqrt{\frac{C}{r}}\ln[\chi_{max}+\sqrt{\chi_{max}^2-1}]-\frac{1}{2}, \quad (18)$$

where χ_{max} is to be calculated in the limit $\psi(0)\rightarrow 0$ from Eq. (9). On squaring and expressing in terms of χ_{max}, the latter equation becomes

$$g\psi^2(0)\chi_{max}^4/2 + (r-r_s^2/C)\chi_{max}^2 - [r+g\psi^2(0)/2]=0. \quad (19)$$

One can easily show that this equation has only one real, positive root for χ_{max} [21]. The behavior of that root in the limit $\psi(0)\rightarrow 0$ depends on the sign of the quantity $r-r_s^2/C$. If $r-r_s^2/C\leq 0$, then χ_{max} diverges [i.e., $\psi(L/2)$ tends to a nonzero limit] as $\psi(0)\rightarrow 0$. In such a case, Eq. (18) shows that $H(0,0)$ diverges logarithmically. Therefore, for any r in this range and arbitrary L, there is always a solution to the equation $H(\psi(0),0)=0$ with nonzero values of $\psi(0)$ and $\psi(L/2)$. On the other hand, when $r-r_s^2/C>0$, the solution for χ_{max} remains finite in the limit $\psi(0)\rightarrow 0$. This finite solution for χ_{max} must satisfy the equation comprised of the nonvanishing terms of Eq. (19), namely,

$$(r-r_s^2/C)\chi_{max}^2 - r = 0, \quad (20)$$

and, hence, is given by

$$\chi_{max} = \sqrt{\frac{\tilde{r}}{\tilde{r}-1}}, \quad (21a)$$

where

$$\tilde{r} \equiv \frac{Cr}{r_s^2} = \frac{\xi_s^2}{\xi^2} \propto (T - T^*). \qquad (21b)$$

Setting $H(0,0)=0$ in Eq. (18) with χ_{max} given by Eq. (21a) yields the critical relation between r and L for a given value of the parameter ξ_s. Note that the critical locus in this mean-field theory does not depend on g. Letting L_{cr} denote the critical thickness at which the film disorders, for given temperature and ξ_s, we have

$$\frac{L_{cr}}{\xi_s} = \frac{2}{\sqrt{\tilde{r}}} \ln[\chi_{max} + \sqrt{\chi_{max}^2 - 1}], \qquad (22a)$$

or, equivalently [22]

$$N_{cr} = \frac{2\xi_s}{d\sqrt{\tilde{r}}} \ln\left[\frac{\sqrt{\tilde{r}} + 1}{\sqrt{\tilde{r}} - 1}\right], \qquad (22b)$$

where $N_{cr} = L_{cr}/d$. For a fixed temperature, L_{cr} is the maximal thickness for which the film exhibits smectic ordering. Note that L_{cr} approaches infinity at the temperature T_s for which $\tilde{r} = 1$, given by

$$T_s = T^* + \frac{r_s^2}{Ca}. \qquad (23)$$

(Despite the fact that T_s is quadratic in r_s, this expression is only valid for negative r_s.) These results imply that, according to the present theory, a smectic film of arbitrary thickness is stable relative to a film of isotropic liquid in the temperature range $T < T_s$, where T_s is larger than the bulk mean-field transition temperature T^*. Thus we obtain the interesting outcome that the surface-induced stability of the film does not vanish with increasing film thickness. This is due to the fact that, for $T^* \leq T \leq T_s$, $\psi(0) \to 0$ as $L \to \infty$, so that there is no bulk free-energy penalty for forming a smectic film of arbitrary thickness [25]. This result in turn suggests that, depending on the experimental conditions, measurements of the "bulk" smectic transition temperature may in fact detect T_s rather than the true transition temperature T^*.

Here we compare the predictions of Eq. (22b) with the experimental data of [5] for the compound 5O.6, which exhibits a very weak first-order SmA-N phase transition and was reported to be well-fit by the power law $L_{cr} = l_0 (T/T_0 - 1)^{-\nu}$ with fitting parameters $T_0 = 60.35\,°\text{C}$, $\nu = 0.82$, and $l_0 = 1.2$ nm. Although Eq. (22b) has a different functional dependence, it also fits the reported experimental data [5] very well and with the same number of fitting parameters. For fitting purposes, we can express $\tilde{r} = (T - T^*)/(T_s - T^*)$. Figure 2 compares the power-law fit, represented by the triangles, with that obtained using Eq. (22b) (solid line), where the best-fit parameters are found to be $2\xi_s = 189.52$ nm, $T^* = 59.53\,°\text{C}$, and $T_s = 60.58\,°\text{C}$. Note that the *fitted* divergence temperatures T_0 and T_s are quite close. In [5], the observed bulk SmA-N transition temperature T_{AN} was reported to be $60.50\,°\text{C}$, in excess of our fitted mean-field transition temperature T^* by approximately $1°$ but almost coin-
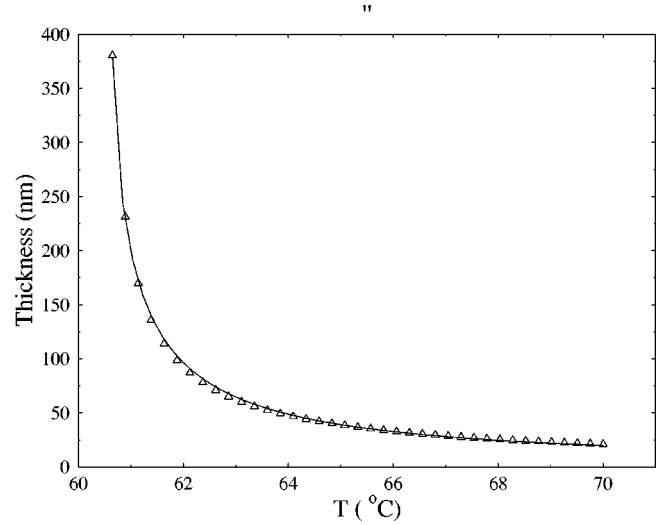

FIG. 2. Comparison of the power-law fit (triangles) [5] with the fit of Eq. (22b) for the critical film thickness vs temperature for the compound 5O.6. See the text for values of the fitting parameters.

ciding with T_s. It is worthwhile noting, however, that the bulk transition temperature T_{AN} in [5] was determined by observing changes in the film meniscus. If the meniscus is considered to be a pile of smectic layers of varying step length, then it is plausible on the basis of the present theory to expect that the observed changes in the meniscus occur close to T_s rather than T^*.

One other system with a bulk SmA-N transition has been shown to exhibit layer-thinning transitions [6], but this behavior occurs over a small thickness range, which makes the fitting less reliable than for the data of [5]. Equation (22b) can also be compared with experimental data for layer-thinning transitions in compounds which undergo first-order SmA-I transitions [1–4]. We find that the equation generally fits the data quite well in these cases, with $T_s \approx T_0$ where the latter is obtained from the power-law fit, although resulting in quite large differences ($\approx 5\,°\text{C}$) between the fitting values of T_s and T^*. Such differences could be expected due to the first-order nature of the bulk phase transition, since the mean-field parameter $r = a(T - T^*)$ should remain positive at the bulk transition in such cases. The present model for the bulk free energy in Eq. (2), however, is not applicable without further modification to smectic liquid crystals undergoing first-order transitions, and we cannot make firm conclusions about such cases here.

According to the recent findings in Refs. [12,13], dislocation loops spontaneously develop before the smectic order disappears across a film which undergoes layer thinning. This implies that the film "critical" points predicted by Eq. (22a) may be preempted by the growth of such loops, so that Eq. (22a) only provides an upper bound for the true layer-thinning transition temperatures. The next section supports the idea that, according to the present theory, during thinning either the order parameter becomes zero across the film, probably resulting in rupture of the film, or that dislocation loops develop.
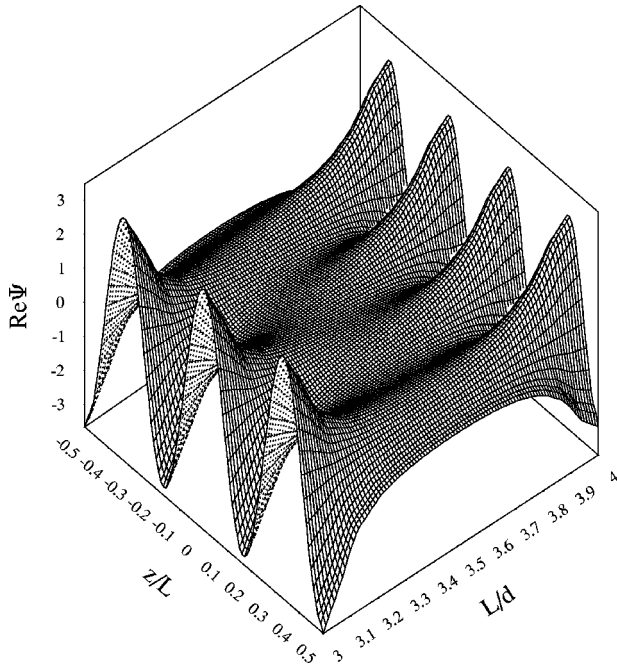
FIG. 3. The de Gennes transition from a four- to three-layer film: $g = r_s = 0$, $h_s = 0.2$, $r = 0.04$, $C = 1$.
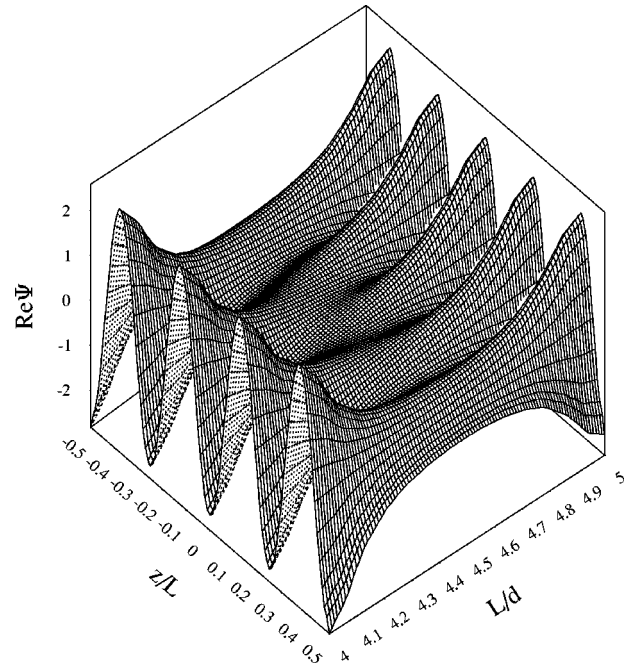

FIG. 4. The de Gennes transition from a five- to four-layer film, with the same parameter values as in Fig. 3.

IV. de GENNES TRANSITION

It was stated by de Gennes [14] that, on varying the film thickness, a continuous transition from N to $(N \pm 1)$ layers can occur without nucleation of dislocation loops in a ''presmectic'' fluid confined between two solid walls. Here we address the question of whether such a continuous transition is possible in the present model for free-standing films. We begin by considering de Gennes' original model [14] in more detail, in which $r_s = g = 0$ and smectic ordering at temperatures above the bulk phase transition ($r > 0$) is due solely to an external field h_s acting at the film surfaces.

Our solutions to the general model (see Sec. II) enable us to find profiles of the density modulation Re Ψ for various thicknesses L. Figures 3 and 4 show the continuous evolution of the profiles as L varies from a four- to three-layer film and from a five- to four-layer film, respectively. The calculations were carried out for $h_s = 0.2$ and $r = 0.04$ (using units for which $C = 1$). If a film with an initially odd number of layers is compressed, the middle layer gradually disappears while the other layers evolve into each other, although some signature of the original middle layer remains for a range of thicknesses less than $(N - 1/2)d$. In contrast to the development of an edge dislocation [16,17], the transition here from N to $(N-1)$ layers takes place throughout the film, leaving it uniform in the (xy) plane. Thinning of an initially even-layer film is different. In this case, the two original middle layers merge into a single layer. An important aspect of these results is that the gradient $\nabla_z u$ of the strain diverges at the film midpoint while the order parameter $\psi(0) = 0$ when $L = (N \pm 1/2)d$ [14]. We will see that the nonlinear term $g\psi^4$ in the bulk free energy does not change these results.

It was argued in [8] that free-standing films containing different numbers of layers correspond to local minima of

the free energy and are ''stabilized'' relative to each other by the presence of sufficiently large metastability barriers. This interpretation was also used in [11], where it is pointed out that the thickness L can be regarded as a free thermodynamic variable and that regions of L with negative second derivative $\nabla_L^2 F_{eq}$ are thermodynamically unstable, since they correspond to a negative effective compressibility modulus. Figure 5 shows the dependence of the free energy on L for $r = 0.04$ (close to the bulk phase transition) and $r = 0.4$ (far from the phase transition) for the original de Gennes model. We note that the analysis presented in [11,14] is only valid for $\xi \ll L$, which corresponds to large r. One sees that the curve for $r = 0.4$ has the cosinelike behavior predicted by de
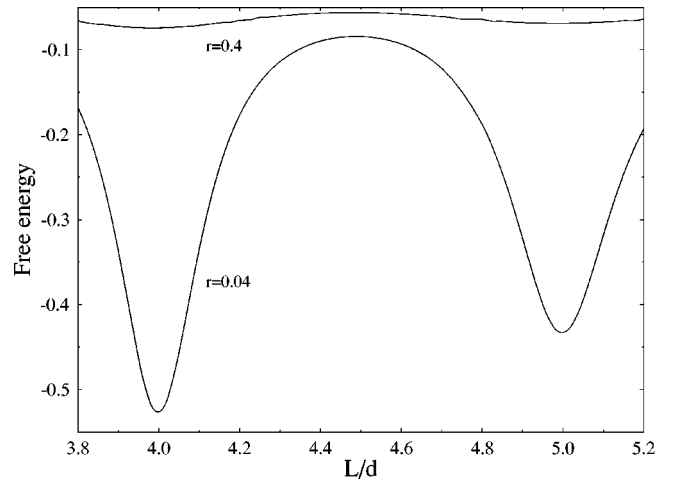

FIG. 5. The dimensionless free energy F (scaled as described in Sec. II) of the de Gennes model ($g = r_s = 0$) for $h_s = 0.2$ and various values of r ($C = 1$).

Gennes [14], with the width of the alternating stable and unstable zones approximately equal to $d/2$ [11]. The regions centered at $L = Nd \pm 0.5d$ are unstable. Figure 5 shows that the zones of stability become narrower and the zones of instability become wider while the amplitude of the oscillations increases with decreasing r.

The occurrence of the continuous ''de Gennes transition'' hinges on being able to achieve a maximum change in thickness $|\Delta L| \equiv |L - Nd|$ equal to $d/2$. Next we examine whether this is possible in the present model for free-standing films.

A. Maximal change in thickness

From Eq. (4b), the relative change in thickness $\Delta L/d$ can be expressed in terms of the strain deformation $u(z)$ as

$$\frac{\Delta L}{d} = \frac{1}{\pi} q_0 u(L/2). \tag{24}$$

Expressing dz in terms of $d\psi$ using Eq. (7), the relation Eq. (5) for $u(z)$ can be written as

$$u(z) = \frac{A\sqrt{C}}{2} \int_{\eta(0)}^{\eta(z)} \frac{d\eta}{\eta \left[\frac{1}{2} g\, \eta^3 + r\, \eta^2 + B\, \eta - A^2 C q_0^2 \right]^{1/2}}, \tag{25}$$

where we defined the new variable $\eta = \psi^2$. Substituting for B from Eq. (8), this becomes

$$u(z) = \frac{A\sqrt{C}}{2} \int_{\eta(0)}^{\eta(z)} d\eta\ \eta^{-1} [\eta - \eta(0)]^{-1/2}$$

$$\times \left[\frac{1}{2} g\, \eta^2 + \left(r + \frac{1}{2} g\, \eta(0) \right) \eta + \frac{A^2 C q_0^2}{\eta(0)} \right]^{-1/2}. \tag{26}$$

Hence, the change in thickness ΔL is given by

$$\frac{\Delta L}{d} = \frac{A q_0 \sqrt{C}}{2\pi} \int_1^{\chi_{max}^2} dx\ x^{-1} (x - 1)^{-1/2}$$

$$\times \left[\frac{1}{2} g\, \eta^3(0) x^2 + \left(r + \frac{1}{2} g\, \eta(0) \right) \eta^2(0) x + A^2 C q_0^2 \right]^{-1/2}, \tag{27}$$

where $x = \eta(z)/\eta(0)$ and $\chi_{max}^2 = \eta(L/2)/\eta(0)$ as earlier. Due to r and g being positive, an upper bound on the thickness change is obtained in the limits $\eta(0) \to 0$ and $\chi_{max} \to \infty$. This yields

$$\left(\frac{|\Delta L|}{d} \right)_{max} = \frac{1}{2\pi} \int_1^\infty \frac{dx}{x\sqrt{x - 1}} = \frac{1}{2}. \tag{28}$$

Therefore, regardless of the nonlinear or surface contributions, the magnitude of the thickness change associated with the strain $u(z)$ cannot exceed $d/2$ in our model for free-standing films. In order to achieve the maximum change $d/2$
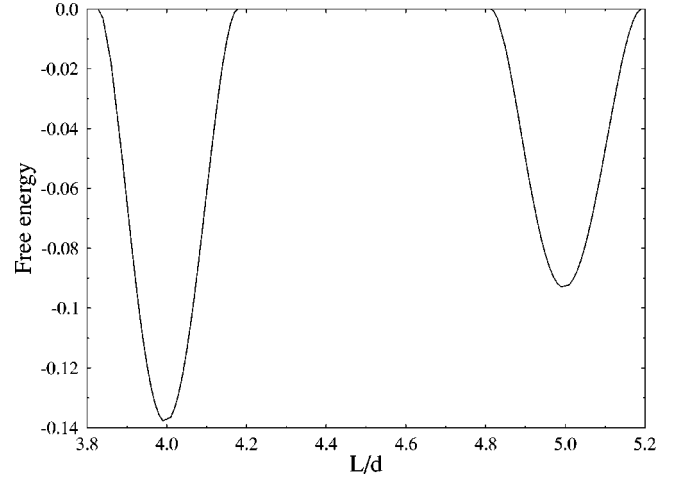

FIG. 6. The dimensionless free energy F (scaled as described in Sec. II) vs thickness L/d for $h_s = 0$, $r_s = -0.2$, $g = 0.04$ and $r = 0.04$, $(C = 1)$.

and hence a continuous transition from N to $N \pm 1$ layers in the sense of de Gennes, it is necessary that $\psi(L/2)$ remains nonzero as $\psi(0) \to 0$, so that $\chi_{max} \to \infty$.

An analysis of our more general model shows that, if $h_s > 0$, then $\psi(L/2)$ always remains nonzero as $\psi(0)$ tends to zero and therefore that $|\Delta L|/d$ can reach $1/2$. On the other hand, if $Cr > r_s^2$ and $h_s = 0$, then the ratio $\psi(L/2)/\psi(0) \equiv \chi_{max}$ remains finite as $\psi(0)$ tends to zero. In these circumstances, $(|\Delta L|/d)_{max} < 1/2$ and a continuous transition from N to $(N \pm 1)$ layers is impossible. When the change in thickness reaches its maximal values, the smectic order vanishes over the width of the whole film and the film free energy tends to zero. Figure 6 shows the dependence of the free energy F on layer thickness L/d, indicating that there are ''absolutely forbidden'' regions of the thickness L, where the free energy equals zero, which separate films of thicknesses Nd and $(N \pm 1)d$. These findings show that a continuous de Gennes transition from N to $(N \pm 1)$ layers is possible only if $h_s > 0$. Otherwise, when the thickness reaches the forbidden zones, either the smectic order parameter becomes zero across the whole film, probably resulting in film rupturing, or dislocation loops develop. The present considerations cannot distinguish between these scenarios, which require a dynamical treatment allowing for inhomogeneities in the plane of the film.

V. DISCUSSION

In summary, we have modified de Gennes' theory [14] of a ''presmectic'' fluid confined between two walls, generalizing the surface contribution to the free energy by including quadratic terms in the surface order parameter $\psi(\pm L/2)$. The coefficient r_s of these terms is considered to be an intrinsic property of the liquid-crystalline material. In contrast with theories which attribute surface-induced smectic-A ordering to external-field-like coupling terms [7,14], the present model always exhibits a trivial solution corresponding to the absence of any smectic ordering. For negative values of r_s, films with smectic order can be stabilized for a finite range of

temperatures above the bulk transition temperature. Therefore, the present theory attributes the distinction between smectic materials which exhibit layer-thinning phenomena and those which do not to the sign of the surface coupling constant r_s. An interesting and unexpected finding is that $T_c(N)$ tends to a value $T_s > T^*$ rather than to the bulk transition temperature T^* with increasing N, and that films of arbitrary thickness can be stabilized at all temperatures $T \leq T_s$. This persistent finite-size effect is due to the fact that surface-induced smectic ordering below T_s is confined to a surface region of characteristic length ξ_s and produces no bulk free-energy penalty in the limit of infinite thickness L.

In the original de Gennes model [14], a presmectic film can have a thickness L different from Nd, and the dilation or compression of the film can be as much as half the smectic layer spacing, which allows for a continuous transition from N to $(N \pm 1)$ layers. We have analyzed the maximal compression and dilation which can occur in the present model, and found that such a continuous transition is only possible when the external field h_s is nonzero. Films with free surfaces, for which we have argued that $h_s = 0$, cannot have arbitrary values of the thickness due to the existence of forbidden zones that divide the allowed zones centered at $L = Nd$. The smectic order parameter vanishes across the film as the thickness approaches the edges of the allowed zones, which we presume must lead either to film rupture or to the nucleation of dislocation loops. The latter possibility accords with the recent experimental observations of dislocation loops during thinning transitions [13,12]. It is plausible that such a nucleation process starts when the difference between the depths of the free-energy wells for $N+1$ and N-layer films (see Fig. 6) becomes larger than the free-energy cost (per unit area) due to the line tension associated with the dislocation loops [23,24].

Although the origin of the surface parameter r_s is beyond the scope of this paper, several plausible mechanisms for it can be envisioned. One is due to coupling between orientation-dependent molecular interactions and translational symmetry breaking at the free surfaces of the film [9]. Fluctuation effects could also play a role, as first pointed out by Selinger and Nelson [26] in a related context. Fluctuations of the smectic layers can affect the observed smectic order parameter $\psi(z)\exp[-q_0^2\langle u(z)^2\rangle/2]$ by quenching the mean-square fluctuations $\langle u(z)^2\rangle$ of the layer-displacement field $u(z)$ near the surfaces, due to the presence of surface tension [27–29]. These fluctuation effects are not yet fully understood, but might be represented by corrections to the temperature variable r. In the smectic phase, the mean-square fluctuation $\langle u^2 \rangle$ has a profile [27–29] which is flat in the middle of a film and very steep near the film surfaces, which implies that there is an effective correction to r which is localized at the surfaces and hence represented by the surface coupling constant r_s.

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