PHYSICAL REVIEW E VOLUME 53, NUMBER 3 MARCH 1996

Metastability of freely suspended liquid-crystal films

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(Received 2 August 1995)

We investigate the conditions required for the existence of smectic-A liquid-crystal films freely suspended in vapor. This work is based on a molecular density-functional theory developed in earlier studies of wetting and layering transitions of smectic-A films at liquid-solid and liquid-vapor interfaces. It is emphasized that all freely-suspended films are metastable with respect to either the absence of the film or the formation of the bulk smectic phase, depending on the relative stability of the bulk vapor and smectic phases. Films containing different numbers of layers correspond to *local minima* of the grand canonical potential, and are "stabilized" relative to each other by the presence of sufficiently large metastability barriers. The disappearance of these barriers corresponds physically to the "rupturing" of the films. It is demonstrated that surface enhancement of smectic ordering does not play an essential role in the existence of freely suspended films, but may influence the order of disappearance of the layer-layer metastability barriers on changing temperature. We relate these findings to the results of recent experimental studies of "layer thinning transitions" in freely suspended films.

PACS number(s): 61.30.Cz, 64.70.Md, 68.45.Gd

I. INTRODUCTION

Among the many important and interesting properties exhibited by liquid-crystal (LC) materials, one of the most novel is the ability of smectic phases to form freely suspended (FS) films under appropriate conditions. For several years, such films have been the focus of considerable experimental and theoretical study, aimed primarily at understanding the effects of reduced dimensionality and surface-enhanced ordering on LC phase transitions [1–6]. In the more recent of these studies [4–6], the latter effects have been connected to interfacial wetting phenomena.

Despite the work cited above, there remain fundamental questions concerning the existence and stability of freely suspended smectic (FSS) films [7]. It has sometimes been asserted that the stability of such films is due to their surface tension γ [7,8]. This statement by itself has little meaning, however, since ordinary liquids or nonsmectic LC phases should then be just as capable of forming FS films, in contrast to most observations. In a few studies, FS films have been obtained using *nematic* LC's [9,10], but these have only been observed within a very narrow range of temperatures above the smectic-nematic transition temperature. More properly, it can be said that the proximity of surfaces may enhance the stability of smectic phases relative to other less-ordered phases. This arises from various surface-induced effects, related both to increased orientational ordering [11] and the suppression of smectic elastic fluctuations [12]. While these effects probably contribute, they do not fully account for the particular stability of FSS films.

FSS films are examples of "black films" and are considered to be thermodynamically *open* systems [7,13,14], able to exchange molecules with a reservoir (i.e., the film meniscus) and thus characterized by a fixed chemical potential μ. As such, the thermodynamically stable states of the system are those that minimize the interfacial excess grand canonical potential $\Delta\Omega = \Omega - \Omega_V = \gamma A$, where Ω is the total grand potential, Ω_V is the grand potential of the bulk vapor in equilibrium with the film, and A is the fixed area of the film. Experimentally, it is found that the surface tension (more properly called the film tension) γ of a FSS film is positive [7,8]. But this implies that any FSS film is only *metastable*, as the absolute minimum of the excess grand potential can then be achieved by the absence of the film, for which $\Delta\Omega = 0$. The conclusion that FSS films are only metastable thermodynamically is not new: for example, it is contained implicitly in the argument of Prost [15] about the limited lifetimes of these films, based on considering the free-energy barrier for nucleation of a "hole" in such a film [16].

This suggests that one should view a sequence of FSS films, differing in thickness from each other by integral numbers of layers, as a sequence of thermodynamically metastable states. *The existence of such a discrete sequence of metastable states is a natural consequence of the "quantized," i.e., layered, structure of a smectic phase.* What we describe in the remainder of this paper is the elaboration of this picture at a mean-field level of approximation. This is based on calculations using a density-functional theory developed in previous work to examine wetting and layering transitions in smectic-A (Sm-A) films adsorbed at liquid-vapor and liquid-solid interfaces [17,18]. In the present work, we study solutions of the theory that represent planar suspended Sm-A films of variable thickness in equilibrium with an infinite vapor phase. These discrete structures correspond to *local minima* of the grand potential functional, separated from each other by metastability barriers, and are shown to be globally metastable with respect to either the absence of any such film *or* the formation of the bulk Sm-A phase, depending on the relative stability of the bulk vapor (denoted V) and Sm-A phases. The connection to wetting behavior at interfaces between bulk V, Sm-A and isotropic liquid (I) phases is also discussed. In the final section of the paper, we discuss the relationships between the present findings and recent experimental evidence of "unusual layer thinning transitions" reported in Ref. [5].

II. THEORY: GENERATION OF FREELY SUSPENDED FILMS

We refer the reader to previous work [17–19] for a detailed description of the density-functional theory used in the present study. The intermolecular pair potential is taken to consist of a hard-spheroid repulsive core, with major and minor diameters labeled $\sigma_{\|}$ and $\sigma_{\perp}$, respectively, and a long-range attractive potential. The latter in turn contains both a spherically symmetric component (of well depth ϵ_1) and two orientation-dependent interactions (whose strengths are denoted ϵ_2 and ϵ_3) which, respectively, favor nematic and smectic-A ordering. Combining a mean-field approximation for the contribution of the attractive interactions and a "weighted-density" treatment of the repulsive-core contribution, the total grand canonical potential Ω is obtained as a functional of two coupled spatially varying densities. These are the number density $\rho(z)$ and the orientational order parameter $\eta(z) = \langle P_2(\cos\theta)\rangle/\rho(z)$, where the angular brackets denote thermal averaging and θ is the angle between a molecular axis and the z direction, which is assumed to be normal to the film plane. The equilibrium structure of the system is determined by functional minimization of Ω with respect to $\rho(z)$ and $\eta(z)$. As in Refs. [17] and [18], space is discretized in the z direction using a fine mesh, and the minimization with respect to $\rho(z)$ and $\eta(z)$ at every mesh point is performed using the conjugate-gradient algorithm. The calculations in the present work differ from those in Refs. [17] and [18] in that we impose the boundary conditions $\rho(z) \to \rho_V$ and $\eta(z) \to 0$ in the limits that z approaches both $+\infty$ and $-\infty$, where ρ_V is the number density of the bulk vapor (which is determined by the chemical potential μ and temperature T), as is appropriate for representing a planar film suspended in vapor. In practice, $\rho(z)$ and $\eta(z)$ are assumed to equal the bulk vapor values beyond a finite distance $|z_{\max}|$.

Consistent with the boundary conditions and the absence of external potentials, one solution of the minimization algorithm is the trivial one in which the vapor phase fills all space, $\rho(z) = \rho_V$ and $\eta(z) = 0$ for all z. The corresponding value of the grand potential is denoted Ω_V. We have searched for other nontrivial stationary solutions by "seeding" the numerical iteration procedure with initial $\rho(z)$ and $\eta(z)$ profiles that mimic smectic layers localized near $z = 0$. Depending on the values of the molecular potential parameters and thermodynamic state conditions T and ρ_V, the iterations converge either to the trivial homogeneous solution or to a layered structure. An example of the converged profiles corresponding to a five-layer film is shown in Fig. 1. Such stationary profiles can then be used as initial guesses for searches under other parameter or state conditions. As in our previous work on the development of smectic layers at a wall-liquid interface [18], whenever conditions allow the formation of layers, we generally can obtain several distinct simultaneous solutions of the theory, representing films that differ by integral numbers of layers. The relative stability of these different film states is indicated by the corresponding values of the excess grand potential per unit area, $(\Omega - \Omega_V)/A = \gamma$.

We have studied the stability behavior under variations of the thermal and molecular parameters over ranges similar to those found in Ref. [18] to generate layered films at a wall-liquid interface. We will also confine our attention to parameter ranges in which the bulk V, I, and Sm-A phases are near or at *three-phase* coexistence with each other. [For details of the bulk phase diagrams produced by the present theory, see Ref. [19]. In all present calculations, we have fixed the hard-core anisotropy at the value $\sigma_{\|}/\sigma = 1.8$ used in Ref. [18], where $\sigma = (\sigma_{\|}\sigma_{\perp}^2)^{1/3}$ is a mean hard-core diameter.] Our basic findings about the film stability behavior are illustrated in Figs. 2 and 3, which plot the film tension as a function of film thickness for several fixed sets of values of the thermal and molecular parameters, analogous to the method used for analyzing wetting behavior at interfaces [18]. The measure of film thickness used in Figs. 2 and 3 is expressed by the integrated order parameter,

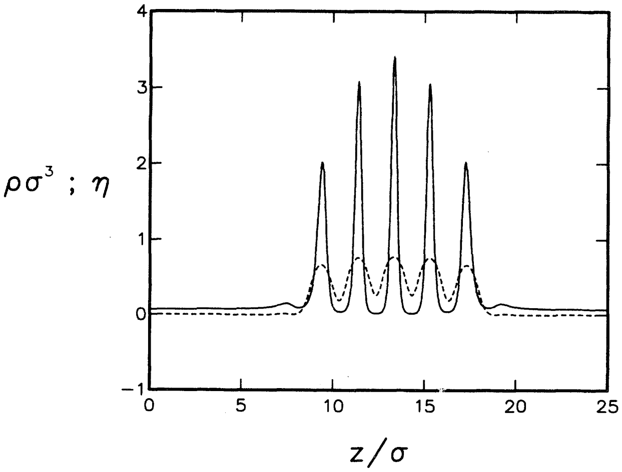

FIG. 1. Profiles of the number density (solid line) and orientational order parameter (dashed line) of a five-layer film at the V-I–Sm-A triple point.

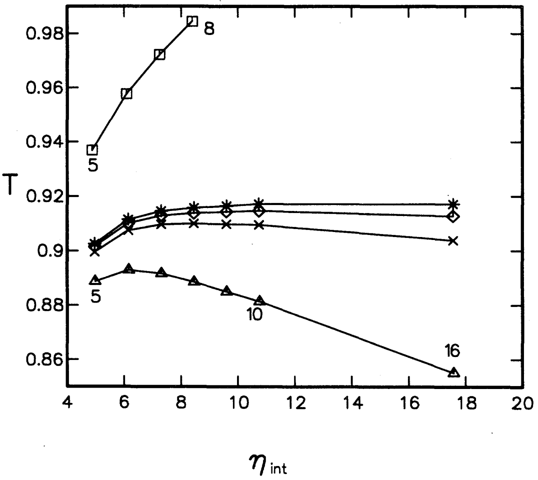

FIG. 2. Curves of reduced film tension vs integrated order parameter. The lines are only a guide to the eye, while the discrete points correspond to the actual values of γ obtained for films with the indicated numbers of layers (see text). From top to bottom, the values of $|\epsilon_3|$ corresponding to the curves are 0.675, 0.6786, 0.6787, 0.6789, and 0.68.

$$\eta_{\rm int} = \int_{-\infty}^{\infty} dz\eta(z). \tag{1}$$

The particular results shown in the figures correspond to fixed values of $T = 0.31$, $\rho_V = 0.07049$, and $\epsilon_2 = 0.43$ (in units of ϵ_1/k_B, σ^{-3}, and ϵ_1, respectively), and for several different values of ϵ_3. For these values of the fixed parameters, and when $|\epsilon_3|$ is sufficiently small, the bulk vapor is at coexistence with the *isotropic* liquid phase. For larger values of $|\epsilon_3|$, however, the bulk smectic-A phase becomes more stable than either the V or I phases. As discussed shortly, this transition in the bulk phase stability accounts for the gross variations of the curves in Figs. 2 and 3. The discrete points on the curves in these figures correspond to the final stationary values of γ for films containing the indicated numbers of layers, while the smooth lines joining the points are only to guide the eye. As in analogous graphs discussed in Ref. [18], it is expected that the discrete points are actually separated by metastability barriers, i.e., local *maxima* in γ, but the latter are not associated with well-defined physical structures and our calculations do not produce them.

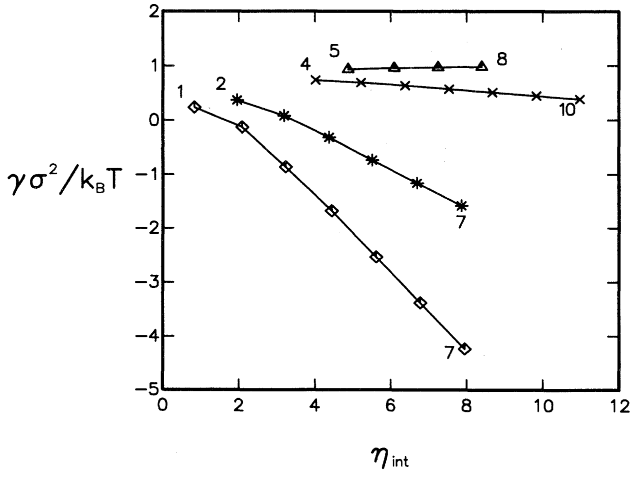

FIG. 3. Same as Fig. 2, but for a wider range of $|\epsilon_3|$ values. From top to bottom, these values are 0.675, 0.7, 0.8, and 0.9.

For the smaller magnitudes of $|\epsilon_3|$ between 0.675 and 0.68, shown in Fig. 2, nontrivial solutions are obtained only for films containing a minimum of five smectic layers. In these cases, if the minimization algorithm is started with an initial iterate containing a smaller number of layers, the algorithm always converges to the homogeneous vapor state. This corresponds physically to the spontaneous "rupturing" of such thin films. As $|\epsilon_3|$ is progressively increased, the minimum number of layers that can be "stabilized" is reduced successively from five to one, as shown in Fig. 3. However, in the latter cases the stable bulk phase is smectic-A rather than vapor, and FSS films of all thicknesses are unstable relative to the bulk Sm-A phase. The bulk transition from V to Sm-A is reflected by the sign of the slope of the *asymptotically linear* variation of γ with film thickness. This asymptotic behavior is easily understood from the fact that, for large thickness L (which should then be proportional to $\eta_{\rm int}$), the system approaches that of a bulk Sm-A phase sandwiched between two V–Sm-A interfaces. Therefore, in the large thickness limit, the excess grand potential per unit area should be given by

$$\gamma \approx 2\gamma_{VA} - \Delta P L, \tag{2}$$

where $\Delta P = P_A - P_V$ is the difference between the pressures of the bulk Sm-A and V phases (both characterized by the same chemical potential μ) and γ_{VA} is the interfacial tension of a single interface between these two bulk phases. The asymptotic slope of a film-tension curve is thus controlled by the relative stability of the bulk phases, the more stable phase having the larger pressure. When the smectic-A phase is more stable, the film tension γ inevitably becomes *negative* for sufficiently large thickness L, and the minimum grand-potential state of the system is that in which the Sm-A phase fills all space. When the bulk vapor phase is more stable, the film tension asymptotically *increases* with thickness L and thus becomes increasingly unstable relative to the absence of any film.

Details of the behavior near the bulk transition are shown in Fig. 2. At bulk V–Sm-A coexistence, $\Delta P = 0$ and the film tension asymptotically approaches the constant value $2\gamma_{VA}$. We associate this situation with that physically realized in most experiments [8]. In Fig. 2, this is seen to occcur for $\epsilon_3 = -0.6786$. For values of $|\epsilon_3|$ smaller than this, the film tension increases monotonically with thickness from its value for the five-layer film. For *slightly* larger values of $|\epsilon_3|$, when the bulk smectic-A phase is more stable, the film tension exhibits a maximum between five and ten layers. This implies the occurrence of first-order transitions between films with different numbers of layers, when two such films have equal values of γ. However, both such "coexisting" films are unstable relative to the bulk smectic-A phase. We cannot rule out the possibility of more complex behavior of the γ vs L curves on using either a different molecular model or a different theoretical method. For example, in the most experimentally relevant case of bulk V–Sm-A-coexistence, we can envision nonmonotonic variation and/or a *negative* initial slope of γ vs L.

One other property revealed by Figs. 2 and 3 concerns the "penetration length," i.e., the distance into the film beyond which surface effects become negligible. It is plausible to associate the penetration depth with half the value of the thickness L beyond which γ obeys the linear variation in Eq. (2). From the curves in Fig. 2 near bulk V–Sm-A-coexistence, this appears to occur at film thicknesses slightly greater than ten layers. We note that the relative variation of γ between the minimum-thickness five-layer film and the asymptotic linear regime is very small, about 2%. In their initial measurements of the film tension, Stoebe *et al.* [8] found that γ was practically constant for films varying in thickness from two up to around 100 layers, within an experimental resolution of about 5%, which was remarked to be "surprising." In more recent experiments, the film tension was found to be independent of thickness within a resolution as small as 1% [20]. We believe that refinements to the present theory may reduce the predicted variation in γ to levels that are consistent with these experiments.

Experimentally, at bulk V–Sm-A-coexistence, it is usually found that FSS films can exist down to thicknesses of two layers, while single-layer films rupture spontaneously [1-8,15]. As noted, the minimum film thickness that we have obtained at bulk coexistence is five layers. This may be related to the absence of surface-enhanced smectic ordering in our theory, as will be discussed in the next section. Nonetheless, the existence of a finite lower thickness limit for FSS films is a qualitatively correct prediction of the theory.

III. CONNECTION TO WETTING BEHAVIOR

In this section we investigate whether there is any surface-enhanced stabilization of the smectic-A phase in films relative to less-ordered phases, i.e., isotropic (I) or nematic (N) liquid. To examine this we shall consider the wetting behavior of interfaces between the *bulk* Sm-A, I and V phases, choosing parameter ranges such that the N phase does not become stable in bulk. Using Eq. (2), we can obtain the interfacial tension γ_{VA} on letting $L \to \infty$ at bulk V–Sm-A-coexistence. In practice, as noted earlier, the film tension under these conditions becomes essentially constant for thicknesses greater than ten layers, but we have verified the following results using films as large as 20 layers thick. Alternatively, one could, in principle, calculate γ_{VA} by generating an interface between the semi-infinite bulk phases, as was done in Ref. [17] for the case of the V–I interfacial tension γ_{VI}. This approach is problematic, however, as first pointed out by Widom [21] in a slightly different context, due to an ambiguity in the interfacial tension obtained in this manner when either of the coexisting phases is spatially modulated. The present approach, which is based on considering the limiting behavior of thin films, does not exhibit the ambiguity described by Widom, since the method does not entail subtracting the grand potential of the bulk modulated (i.e., smectic-A) phase.

By an analogous method, generating smectic-A films suspended in the bulk *isotropic liquid* rather than vapor, we can calculate the interfacial tension γ_{IA} between coexisting I and Sm-A-phases. Choosing state conditions so that the vapor and isotropic liquid are also in coexistence with each other, as applies to the curves in Figs. 2 and 3 at sufficiently weak $|\epsilon_3|$, we are thus able to obtain the three sets of interfacial tensions γ_{VA}, γ_{IA}, and γ_{VI} (the latter calculated as in Ref. [17]) required for determining the wetting behavior. Figure 4 illustrates the determination of γ_{VA} and γ_{IA} by extrapolation of the film-tension curves to large L.

Table I summarizes our results at fixed temperature $T = 0.31$ and for several different values of the parameters ϵ_2 and ϵ_3, which are varied simultaneously in such a way as to maintain three-phase coexistence of the vapor, isotropic liquid, and smectic-A phases. The table also lists the values of two "spreading coefficients" defined by

$$S_I = \gamma_{VA} - (\gamma_{VI} + \gamma_{IA}), S_A = \gamma_{VI} - (\gamma_{VA} + \gamma_{IA}), \quad (3)$$

which are used to characterize wetting of the V–Sm-A-interface by the isotropic liquid and of the V-I interface by the smectic-A phase, respectively. [Note that $S_I - S_A = 2(\gamma_{VA} - \gamma_{VI})$.] In all cases, we see that $S_I > S_A$ ($\gamma_{VA} > \gamma_{VI}$), which indicates that the vapor phase prefers contact with the isotropic liquid rather than with the smectic phase, i.e., the isotropic liquid partially wets the V–Sm-A interface while there is *nonwetting* of the V-I interface by the smectic-A phase. One trend indicated in Table I is that S_I increases monotonically with increasing ϵ_2 (decreasing $|\epsilon_3|$), which suggests that wetting by the isotropic liquid could become complete, i.e., $S_I \to 0$, at larger values of ϵ_2, although this might be pre-

TABLE I. Variation of reduced interfacial tensions and spreading coefficients with molecular parameters at fixed temperature $T = 0.31$.

ϵ_2	ϵ_3	γ_{VA}	γ_{IA}	γ_{VI}	S_I	S_A
0.30	-0.8529	0.4274	0.3693	0.1031	-0.045	-0.6936
0.43	-0.6786	0.4586	0.3855	0.1034	-0.0304	-0.7407
0.50	-0.5747	0.4448	0.3562	0.1035	-0.0149	-0.6975

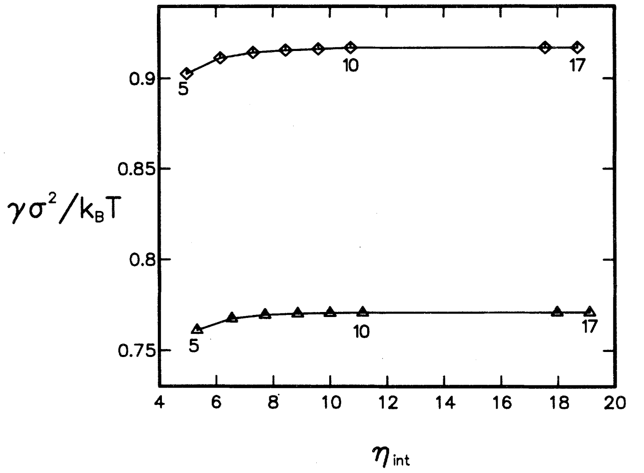

FIG. 4. Curves of reduced film tension vs $\eta_{\rm int}$ at the bulk V-I–Sm-A triple point, $T = 0.31$, $\epsilon_2 = 0.43$, and $\epsilon_3 = -0.6786$. The upper and lower curves correspond to smectic-A films suspended in vapor and isotropic liquid, respectively.

empted by the eventual bulk transition to the nematic phase. We have not pursued this question, as we are more interested in determining whether any conditions favor the possibility of partial wetting by the smectic-A phase.

Before considering the latter question, we briefly note two other trends indicated by the data in Table I. Both γ_{VA} and γ_{IA} exhibit weak maxima as functions of ϵ_2 or ϵ_3, while γ_{VI} remains practically constant. The behavior of the latter is not surprising, since the degree of both orientational and smectic order at the V-I interface is quite weak and is only slightly modified by the changes in ϵ_2 and ϵ_3 [17]. The occurrence of the maximum in γ_{IA} (and hence in γ_{VA}) is likely caused by a subtle competition between "orientational" and "smectic" ordering under the present parameter variations. Both contributions to Ω, i.e., the terms directly proportional to ϵ_2 and $|\epsilon_3|$, respectively, are expected to be negative. Thus, in order to maintain bulk coexistence, if ϵ_2 is increased $|\epsilon_3|$ must be decreased and vice versa. The effect of this competition at the interface plausibly may lead to nonmonotonic behavior of γ_{IA}.

The nonwetting of the V-I interface by smectic-A disagrees with our earlier conclusion in Ref. [17] that the Sm-A phase *partially wets* the V-I interface, which requires $S_A > S_I$ or $\gamma_{VA} < \gamma_{VI}$. The conclusion of Ref. [17] was based on the observation of weak oscillations in the profiles of $\rho(z)$ and $\eta(z)$ at the V-I interface, implying that a weak degree of smectic ordering is induced at that interface. It now appears that such weak smectic-A ordering is not sufficient to produce partial wetting by the Sm-A-phase, according to our present results for the interfacial tensions. We have studied the behavior under a wider range of parameter variations, intermediate between the values used in Table I and those considered in Ref. [17], but no qualitative differences have been found. This is indicated in Table II. Here the temperature T is systematically lowered while the parameters ϵ_2 and ϵ_3 are adjusted to maintain three-phase V-I–Sm-A coexistence as before while also approximately maintaining a constant value of $\Delta\epsilon_2 = \epsilon_{2,t} - \epsilon_2$, where $\epsilon_{2,t}$ is the value of ϵ_2 that would produce a V-I-N triple point at the given temperature for sufficiently weak $|\epsilon_3|$. In the present theory, $\epsilon_{2,t}$ depends only on temperature, and the condition of constant $\Delta\epsilon_2$ is imposed in order to reduce any influence on wetting properties from the onset of bulk nematic ordering. As before, it is still found that $\gamma_{VA} - \gamma_{VI}$ is positive and there remains nonwetting by the smectic-A phase. While the table indicates that the difference $\gamma_{VA} - \gamma_{VI}$ is reduced with lowering temperature, the trends suggest that it only approaches zero at unphysically low temperatures.

IV. LAYER-THINNING TRANSITIONS

A recent article by Stoebe *et al.* [5] reported observing "unusual layer-thinning transitions" in FSS films heated above the I–Sm-A transition temperature T_{IA}. In summary, it was found that such films would remain stable above T_{IA} without spontaneously rupturing. Instead, as the temperature was progressively raised, a film underwent a sequence of layer-by-layer "melting" transitions, producing discrete reductions in thickness as the resulting isotropic liquid was absorbed by the bulk reservoir surrounding the film. It was suggested that the layer melting transitions occur in the *interior* of a film rather than at the vapor interface, based on assuming the presence of surface-enhanced smectic ordering. Two important points are that the films were not observed to spontaneously increase in thickness upon cooling, and that the thinning transitions did not occur spontaneously when temperature was held constant but were only induced by *changes* in temperature.

TABLE II. Variation of reduced interfacial tensions and spreading coefficients with temperature.

T	ϵ_2	$\Delta\epsilon_2$	ϵ_3	γ_{VA}	γ_{IA}	γ_{VI}	S_I	S_A
0.31	0.50	0.0984	-0.5747	0.4448	0.3562	0.1035	-0.0149	-0.6975
0.29	0.43	0.0976	-0.5509	0.4980	0.3580	0.1877	-0.0477	-0.6683
0.25	0.30	0.1033	-0.5109	0.6865	0.3952	0.4350	-0.1437	-0.6467
0.21	0.20	0.1000	-0.4574	1.0338	0.4768	0.8344	-0.2774	-0.6762

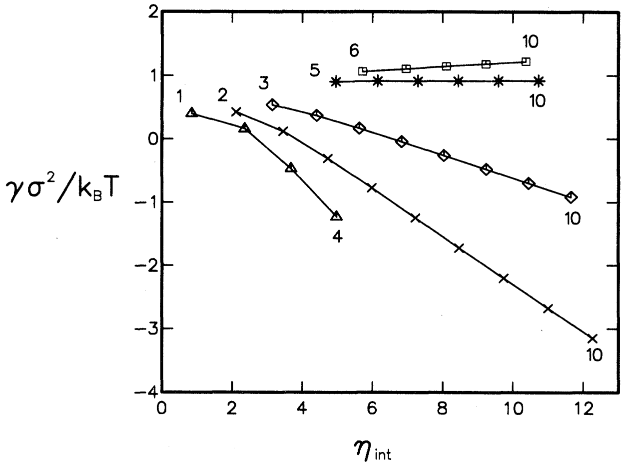

FIG. 5. Similar to Figs. 2 and 3, but showing variation of the film tension as a function of thickness at different temperatures for fixed $\epsilon_2 = 0.43$ and $\epsilon_3 = -0.6786$. From top to bottom, the temperatures are $k_BT/\epsilon_1 = 0.312, 0.31, 0.3, 0.29$, and 0.279.

Can our theory shed any light on these results? In this regard, we are restricted by the fact that the theory does *not* predict a significant degree of surface-enhanced smectic ordering, as indicated by the wetting behavior described in the previous section. We can envision other scenarios, however, due to an improved model or theory, in which surface-enhanced smectic ordering does occur and which could account qualitatively for the observed sequence of layer-thinning transitions with increasing temperature [22]. On the other hand, several key features of the experiment can be explained by the fact that the suspended films are only *metastable.* In particular, the two aspects mentioned in the previous paragraph about nonspontaneity of the growth or reduction of the film on changing temperature suggest that the experiment does not measure true thermodynamic transitions but rather detects the spinodal points or limits of metastability of successive layers of the film.

One other important point about the experimental results of Ref. [5] is that the layer-thinning transitions are only observed for a particular class of partially fluorinated LC's [23]. In all other instances, the authors report that FSS films ruptured at temperatures at or below T_{IA}. *Our theoretical results are fully consistent with the latter behavior.* The curves in Figs. 2 and 3 for variations of $|\epsilon_3| < 0.6786$ apply to FSS films under conditions of bulk V-I coexistence, i.e., when the bulk Sm-A phase is unstable relative to both V and I phases. We have also studied FSS films along a more physically relevant path, fixing ϵ_3 and varying temperature through the V-I–Sm-A triple point. Film-tension curves in the latter case are shown in Fig. 5 and are seen to be very similar to those contained in Figs. 2 and 3. (The thermodynamic path considered here is along the bulk V-I coexistence curve for temperatures $T > T_{IA}$ and its *metastable extension* for $T < T_{IA}$.) With increasing temperature (or decreasing $|\epsilon_3|$), we find that the minimum number of film layers that can be formed progressively increases, and ultimately tends to infinity. This is demonstrated in Fig. 6, which actually plots the maximum temperature at which a film can exist as a function of the film thickness. Most of the temperature range shown in this figure lies *below* the V-I–Sm-A triple point temperature $T_{IA} = 0.31$. Above T_{IA}, films exist only within a very narrow range of temperatures up to the spinodal temperature of the bulk smectic-A phase. It follows from these results that, on increasing temperature, a film of n layers becomes unstable *before* one of $(n+1)$ layers. This means that, if one attempts to raise the temperature in order to melt one layer, the whole film becomes unstable and thus ruptures.

As mentioned in Sec. II, our calculations do not directly reveal any information about the nature of the metastability barriers separating successive local minima of the grand potential Ω, i.e., the "heights" of these barriers and their evolution on variation of the thermal and molecular parameters. We can infer some of this information empirically by detecting the loss of stability of films, as described in the previous paragraph. Additional information can be obtained by viewing the successive iterates of $\rho(z)$ and $\eta(z)$ generated during the conjugate-gradient minimization of Ω (which might be considered as viewing a type of "time evolution" of the profiles). In particular, on raising temperature through a film-instability point, we find that the profile peaks *closest to the interface* (see Fig. 1) always disappear first. This is consistent with our finding of nonwetting by the smectic-A phase [24].

We conclude that the order of disappearance of the metastability barriers between films of different thicknesses is the key to explaining the results of Ref. [5]. What is required is to reverse the order of disappearance from that implied by the present theory, so that the barrier between an n- and $(n+1)$-layer film disappears

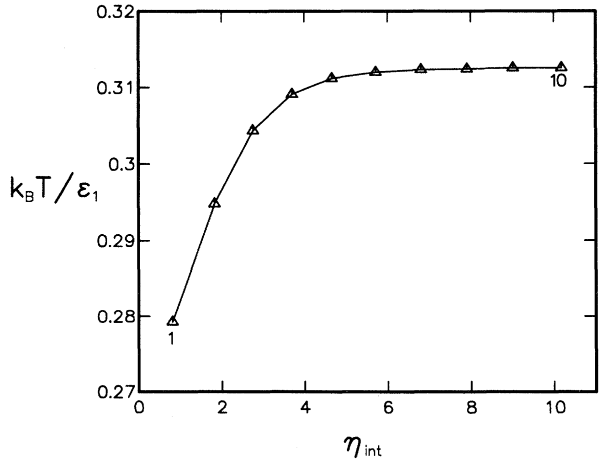

FIG. 6. "Rupturing" temperature of a suspended film as a function of $\eta_{\rm int}$ for $\epsilon_2 = 0.43$ and $\epsilon_3 = -0.6786$. The discrete points are labeled by the number of film layers, and as before the lines are only to guide the eye.

at a *lower* temperature than that between an $(n-1)$- and n-layer film. The variation of the *metastability barriers* with film thickness and state conditions should be distinguished from the variation of the the film tension values at the local minima, such as those displayed in Figs. 2, 3, and 5. It is plausible that a sufficiently strong surface-enhancement of smectic ordering, such as to produce partial or complete smectic-A wetting of the V-I interface, may lead to the desired ordering of the loss of metastability barriers. This is not necessarily sufficient, however, as the more common phenomenon of film rupturing at $T = T_{IA}$ is apparently observed in many LC materials that exhibit partial smectic wetting [5].

Although our findings are inconclusive about the causes of the layer-thinning transitions, we believe that the present work establishes a framework for understanding these transitions, and we hope that it encourages further experimental and theoretical study of this topic.

ACKNOWLEDGMENTS

Y.M. acknowledges partial support from ICI (Spain). A.M.S and L.M. acknowledge support from Grant No. PB91-0090 of DGCyT (Spain). D.E.S. acknowledges financial support from NSERC (Canada). The authors would also like to thank C.C. Huang for bringing Refs. [20] and [23] to their attention.

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[22] For example, successive layer-by-layer thinning transitions could occur on increasing temperature if the film tension at bulk coexistence monotonically *decreases* with thickness rather than increases, as exhibited in Figs. 2 and 3.

[23] A. J. Jin, M. Veum, T. Stoebe, C. F. Chou, J. T. Ho, S. W. Hui, V. Surendranath, and C. C. Huang [Phys. Rev. E (to be published)] have recently reported observing layer-thinning transitions in one other, *nonfluorinated* compound, 54COOBC.

[24] In principle, the location of the layer spinodal points and information about which profile peaks disappear first can be determined from the vanishing eigenvalues and corresponding eigenvectors of the stability matrix $\delta^2\Omega/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')$. Such a calculation appears prohibitive and we believe that our more "empirical" methods described in the text are sufficiently informative. Our conjugate-gradient iterative process may be approximately related to the dynamical evolution of a purely dissipative process controlled by two variables without any conservation law. If any of the variables satisfies a local conservation law, the direction in phase space in which the film becomes unstable may change.