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Surface-enhanced ordering and layer-thinning transitions in freely suspended smectic-*A* films

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We propose a physical mechanism which leads to surface-enhanced smectic-*A* ordering (SESO) at the free surface of a model liquid crystal. We also provide an explanation, based on a density-functional theory, for recent experimental results for the melting behavior of freely suspended smectic (FSS) films. It is shown that stepwise layer-thinning transitions do *not* usually occur during melting of FSS films, despite the presence of SESO. We find that thinning transitions similar to those observed experimentally occur under conditions such that the film interior melts to a nematic rather than isotropic liquid phase. [S1063-651X(97)13202-0]

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Several experimental studies have shown that surface-enhanced ordering can occur at the free surface (i.e., liquid-vapor interface) of liquid-crystal compounds. For example, the nematic (N) phase has been shown to partially or completely wet the interface between the vapor (V) and isotropic (I) liquid phase in compounds of the homologous series nCB for $n=5-8$ [1]. Partial wetting by the smectic-*A* (Sm-*A*) phase, accompanied by several discrete layering transitions on varying temperature, has been observed at the *V*-*I* interface of some higher-*n* homologs of the nCB series [2]. *Continuous* Sm-*A* ordering has also been observed above the bulk *N*–Sm-*A* transition temperature in the compounds 4O.8, 8OCB, and 9CB [3]. Smectic ordering at interfaces has also been investigated theoretically [4–8]. A limitation of the latter studies has been the necessity of applying an *external field* in order to provide sufficiently strong surface-induced ordering to result in Sm-*A* wetting and layering transitions at an interface [7].

Freely suspended films of smectic liquid crystals provide another class of systems in which surface-enhanced ordering effects have been studied [9]. The nature of these films, whose thicknesses can be varied from two up to an arbitrarily large number of layers, is ideally suited for studying the evolution from two- to three-dimensional behavior as well as the effects due to a variable ratio of ‘‘bulk’’ to ‘‘surface’’ interactions. Recently, a type of melting phenomena related to surface-enhanced ordering has been observed in freely suspended smectic (FSS) films. Termed layer-thinning transitions, these were first observed by Stoebe, Mach, and Huang [10] as the stepwise thinning of a FSS film when its temperature was raised above the bulk Sm-*A*–*I* transition temperature T_{AI}. On the presumption that surface-enhanced smectic ordering (SESO) stabilizes the outer layers of the film, the successive thinning transitions were identified with Sm-*A*–*I* transitions of interior layers located at distances beyond some temperature-dependent penetration length from either of the free surfaces bounding the film. A characteristic of these phenomena is that they appear to be fairly rare: so far, such transitions have only been observed in two compounds out of more than 15 examined [10,11], while films of most materials rupture on heating. Recently, layer-thinning transitions have also been reported for compounds in which the bulk Sm-*A* phase transforms to a nematic (rather than isotropic) liquid [12]. The latter work suggested that thinning transitions in these cases might be *universal* phenomena, although this is contrary to the reports of Ref. [11]. So far, no theory has been able to give a clear explanation of these phenomena.

The aim of this paper is twofold. First, we introduce a physical mechanism which leads to SESO within mean-field theory. Second, we provide an explanation of the above results, accounting for the rarity of layer-thinning transitions as well as for similarities in the thinning behavior of films which melt to isotropic and nematic liquids.

The starting point is a density-functional perturbation theory. The reference system is modeled by parallel spheroids of elongation ratio $\sigma_\parallel/\sigma$ whose free energy is obtained from a weighted-density approximation [6]. A standard mean-field approximation is used to evaluate the contribution of the long-range attractive pair potential. The latter is given by

$$\begin{aligned}V_A(12)=&\epsilon_1 V_1(r_{12})+\epsilon_2 V_2(r_{12})\Gamma_2(\theta_{12})\\&+\epsilon_3 V_3(r_{12})\Gamma_3(\theta_1',\theta_2')\\&+\epsilon_4 V_4(r_{12})\Gamma_4(\theta_1',\theta_2',\theta_{12}),\end{aligned}\tag{1}$$

where $r_{12}\equiv|\mathbf{r}_{12}|$ is the intermolecular distance, θ_{12} is the angle between the symmetry axes of molecules 1 and 2, and θ_i' ($i=1,2$) is the angle between the symmetry axis of molecule i and the intermolecular vector $\mathbf{r}_{12}$. The expressions for Γ_n ($n=2,3$) are given in Ref. [7], while

$$\begin{aligned}\Gamma_4=&[2-3\cos^2(\theta_1')-3\cos^2(\theta_2')-3\cos^2(\theta_{12})\\&+9\cos(\theta_{12})\cos(\theta_1')\cos(\theta_2')]/2.\end{aligned}$$

The parameters ϵ_n determine the strengths of the various terms in Eq. (1). This model potential is common to most studies of nonuniform liquid crystals, although not all terms in Eq. (1) are standardly included. In the present work, the functions $V_n(r_{12})$ are given by Yukawa potentials of *differing* ranges, explicitly,

$$V_n(r)=\begin{cases}0, & r<1\\ -\dfrac{1}{r}e^{-\lambda_n(r-1)}, & r>1\end{cases} \tag{2}$$

where distance r is expressed in units of the mean hard-core diameter σ.

The use of different values for the inverse-range parameters λ_1–λ_4 in this model plays a crucial role in promoting SESO at a free surface. This can be rationalized by considering the respective roles played by the interaction terms in Eq. (1). The function $\epsilon_1 V_1(r)$ accounts for isotropic attractive interactions which are responsible for inducing liquid-vapor phase separation and hence for the existence of a liquid-vapor interface. The term $\epsilon_2 V_2(r)\Gamma_2(\theta_{12})$ is analogous to a Maier-Saupe interaction, and therefore induces bulk nematic orientational ordering. The third and fourth terms, proportional to $\epsilon_3 V_3(r)$ and $\epsilon_4 V_4(r)$, respectively, describe coupling between rotational and translational degrees of freedom and induce orientational ordering in the presence of a *nonuniform* density distribution. For sufficiently large $|\epsilon_3|$, the third term is responsible for inducing nematic wetting at a *V-I* interface [1,13] and, in conjunction with spatially anisotropic excluded-volume interactions [6], for stabilizing the bulk Sm-*A* phase. The fourth term, which corresponds to the (222) component in a standard spherical harmonic expansion [14], plays a somewhat similar role to the third term. As the contribution of the last two terms to the free energy is proportional to the density gradient [13], their surface-induced ordering effects are expected to be increased on making the liquid-vapor interfacial density profile sharper, i.e., more abrupt. This can be achieved by reducing the range of the isotropic attractive interaction $V_1(r)$, i.e., by *increasing* λ_1. At the same time, using a *larger* range for the rotation-translation coupling interactions, i.e., reducing λ_3 and λ_4 so that $\lambda_3,\lambda_4<\lambda_1$, enables these interactions to ''sample'' a larger interfacial domain and thus further enhances surface-induced ordering. It is worth mentioning that the importance of using different ranges of the potential terms was not noticed before, to our knowledge, and Lennard-Jones forms have been commonly used for all $V_n(r)$. In this case, increasing ϵ_3 and/or ϵ_4 would promote smectic ordering at the interface, but a stable bulk Sm-*A* phase always occurs before a significant amount of SESO is achieved.

We have confirmed the qualitative reasoning described above by explicit calculations of the interfacial structure and free energy predicted by the theory. For appropriate values of the reduced energy parameters ϵ_n/ϵ_1 and inverse-range parameters λ_n, both partial and complete wetting by the Sm-*A* phase at the interface between coexisting *I* and *V* phases can be achieved, accompanied by discrete layering transitions on varying temperature above T_{AI}. This is, to our knowledge, the first microscopic model able to produce this behavior at a real *V-I* interface. Most details of the wetting properties will be presented elsewhere [15], while here we shall focus on the behavior of FSS films.

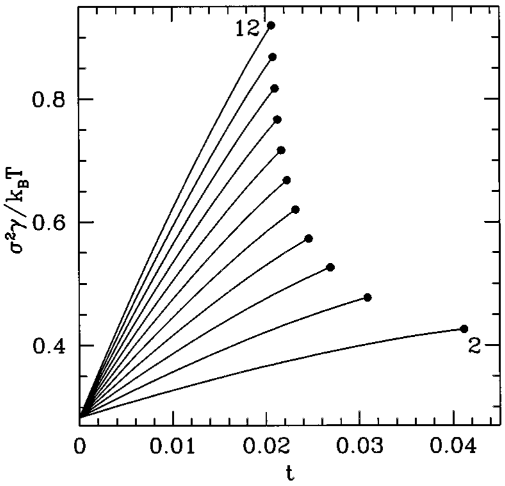

FIG. 1. Reduced film tension vs temperature. The number of smectic layers varies from 12 to 2 as indicated.

Thermodynamically, a FSS film is characterized by its film tension γ [16], which is equal to the excess (relative to bulk vapor) grand canonical potential per unit area. Here we study the behavior of Sm-*A* films at temperatures above T_{AI}, while maintaining bulk *V-I* coexistence. In this region, the bulk Sm-*A* phase is unstable relative to both *I* and *V* phases, hence the film tension should increase with thickness [17]. The behavior is actually plotted in Fig. 1 as γ vs $t\equiv(T-T_{AI})/T_{AI}>0$ for different values of the number of smectic layers n. This shows the generic behavior of films with a significant amount of SESO when the bulk phase diagram contains a *V–I*-Sm-*A* triple point. (The particular set of parameters corresponding to Fig. 1 is $\lambda_1=5$, $\lambda_2=3$, $\lambda_3=\lambda_4=3.5$, $\epsilon_2/\epsilon_1=0.225$, $\epsilon_3/\epsilon_1=-0.110$, $\epsilon_4/\epsilon_1=-0.8$, and $\sigma_\parallel/\sigma=1.8$. The triple-point temperature is $T_{AI}=0.05$, in units of ϵ_1/k_B.) Each curve in this figure ends at the film spinodal temperature T_n, defined as the maximum temperature for which an n-layer FSS film can exist as a *metastable* state [17]. For any fixed value of t, the film tension increases with n. Note that all curves approximately intersect the $t=0$ axis at $\gamma\approx 2\gamma_{VA}$, where γ_{VA} is the interfacial tension of a single interface between bulk *V* and Sm-*A* phases. For large n, T_n approaches increasingly close to the value T_∞ corresponding to the spinodal temperature of the *bulk* Sm-*A* phase on the *V-I* coexistence curve. For the present choice of parameters, the value of T_∞ is 0.051. In this work, films of arbitrarily large n can be generated at all temperatures $T\leqslant T_\infty$, in contrast to the results of a previous theoretical study [17] which did not account for SESO. For all $n\geqslant 12$, the film spinodal temperatures occur within 0.08% of T_∞. For smaller n, the end points begin to deviate significantly from T_∞ and occur at increasingly higher values of t, indicating the increased importance of SESO in thin films.

The absence of any intersections between the γ curves for different n in Fig. 1, except for that at $t=0$, agrees with our earlier assertion [17] that ''layer-thinning transitions'' at $t>0$ cannot be true thermodynamic phase transitions, but rather correspond to the loss of absolute metastability when films are heated through their spinodal temperatures. This figure appears able to account for layer-thinning transitions because, when an n-layer film becomes unstable on being heated through T_n, a local free-energy minimum corresponding to a metastable $(n-1)$-layer film is still available. Whether this minimum will be reached or not depends on the film dynamics. The dynamical behavior is not available from

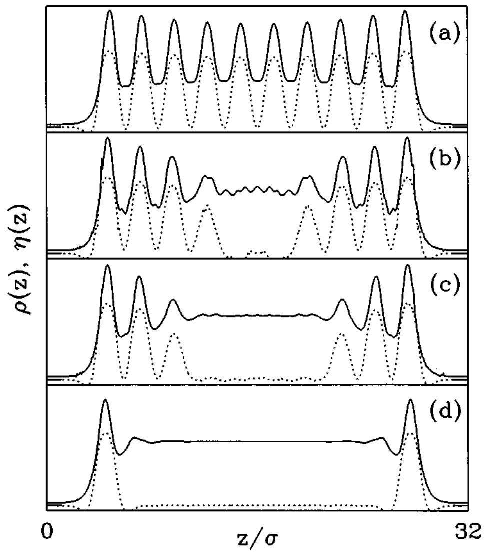

FIG. 2. Density (solid lines) and order parameter (dotted lines) profiles for a ten-layer film. (a) Film structure for reduced temperature 0.051 05 (the film spinodal temperature T_{10}). (b) and (c) Intermediate structures obtained after heating up to $T=0.051\ 06$ during the numerical minimization process, after 160 and 190 iterations, respectively. (d) Final converged profiles.

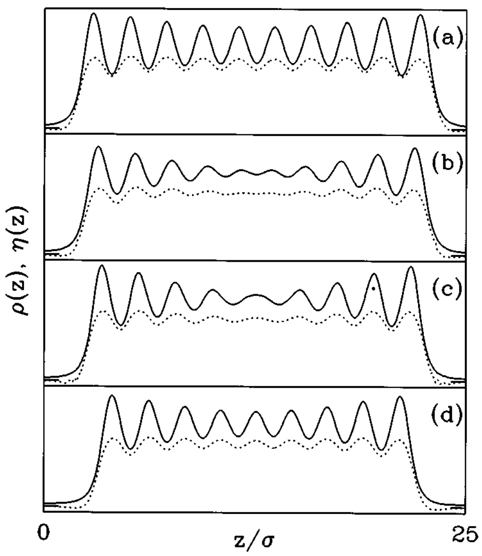

FIG. 3. Same as Fig. 2 but for a ten-layer film whose interior melts into nematic and undergoes a layer-thinning transition to a nine-layer film. (a) Film structure at $T_{10}=0.0654$. (b) and (c) Intermediate profiles generated after heating up to $T=0.0655<T_9$. (d) Final converged profiles corresponding to a nine-layer film at $T=0.0655$.

the present equilibrium theory. However, relevant information is obtained from knowledge of the different spinodal temperatures involved, namely, T_n, T_∞, and $T_{AI}^{(s)}$ this last being the Sm-A–I interface spinodal temperature (such that at $T>T_{AI}^{(s)}$ the outer layers melt and the interface moves toward the smectic region). As surface-enhanced ordering does not appear to be significant at the I–Sm-A interface [15], the relation between the spinodal temperatures must be $T_{AI}^{(s)}<T_\infty<T_n$. This implies that, regardless of the dynamical details, once an interior layer melts into an isotropic liquid, the film subsequently evolves by melting of the remaining smectic peaks rather than by spontaneously compressing. In order to show this behavior, we have studied the evolution of film structure by viewing the intermediate profiles of the number density $\rho(z)$ and orientational order parameter $\eta(z)$ (defined in Ref. [7]) generated during the numerical minimization algorithm [17] when the temperature of an initially metastable film of n layers is raised above the spinodal temperature T_n (Fig. 2) [18].

Several interesting features are revealed by this. The first is that the weak monotonic decay of the profile peaks with distance into the film once more reveals the presence of SESO [Fig. 2(a)]. Second, these results clearly indicate that the film instability occurs by ''melting'' of the interior layers, as hypothesized in experimental studies [10,12], but never confirmed by direct observation. Figures 2(b) and 2(c) show that a region of liquid, characterized by a negligible order parameter $\eta(z)$, develops in the interior of the film and results in the formation of two I–Sm-A interfaces inside the film. This final stage results in either the complete disappearance of the film, i.e., ''rupturing,'' or the formation of a largely isotropic-liquid film with a single smectic peak at each free surface [Fig. 2(d)] [19]. This is probably the usual situation, and explains the experimental findings which indicate that, although SESO is quite common in FSS films, layer-thinning transitions are unusual [10]. We have verified that the behavior of FSS films shown in Fig. 2 is insensitive to whether the Sm-A phase partially or completely wets the V-I interface [15].

We propose a mechanism which accounts for observed layer-thinning transitions and reconciles the experimental findings. We suggest that the interior layers of the film can melt into a *metastable nematic* rather than into the stable isotropic liquid. This possibility is favored in the proximity of a vapor-isotropic-nematic-smectic quadruple point. We have obtained such a state under several different sets of parameters. Here we shall illustrate the generic film behavior using the following set: $\lambda_1=4$, $\lambda_2=3$, $\lambda_3=\lambda_4=4$, $\epsilon_2/\epsilon_1=0.307$, $\epsilon_3/\epsilon_1=-0.655$, and $\epsilon_4/\epsilon_1=0$. The corresponding reduced quadruple temperature is $T_Q=0.065$. We have studied FSS films on raising the temperature above T_Q along the bulk V-I coexistence curve. Now, the interior structure which initially forms on layer melting is nematic (N), characterized by nonzero values of the orientational order parameter, as shown in Fig. 3. It is interesting to note that when n is even, as in the case of Fig. 3, the *two* equivalent middle layers simultaneously melt to a nematic state [Figs. 3(b) and 3(c)], but on further iterations a ''smectic'' layer [exhibiting a peak in both $\rho(z)$ and $\eta(z)$] is *created* as the film compresses itself. This explains the experimental finding [10] that single layers are removed from even-n films despite the equivalence of the two middle layers. The final converged profiles [Fig. 3(d)] correspond to an $(n-1)$-layer film, completing a bonafide layer-thinning transition.

Why does the film in this case evolve by thinning rather than by enlarging the interior nematic region in analogy to Fig. 2? A key difference between the present and earlier case is the *continuous* (or very weakly first-order) nature of the bulk Sm-A–N transition. The near-critical nature of this transition leads, in conjunction with SESO, to ‘‘critical adsorption’’ [20] of the Sm-A phase at the vapor-nematic interface at temperatures near T_Q, a phenomenon characterized by very slow decay of Sm-A ordering away from the free surface. We believe this is the crucial feature which produces an effective attractive interaction between the two interior Sm-A–N interfaces of the film after layer melting and promotes layer thinning.

Variations of the molecular parameters used in Fig. 3 convert the quadruple point into a pair of triple points, which are either a V-I–Sm-A and a I–Sm-A–N triple point or a V-I-N and a V–N–Sm-A triple point [6]. In these two cases, the bulk Sm-A phase melts on heating to either a stable isotropic or nematic liquid, corresponding to the experiments of Refs. [10,11] and [12], respectively. For sufficiently weak perturbations, the layer-thinning behavior shown in Fig. 3 is still obtained. The common feature of layer melting to a *nematic* phase accounts for the similar findings of the two types of experiments.

In summary, we have shown in the context of a mean-field theory that the appearance of SESO at the free surface of a liquid crystal is related to the presence of *differing* ranges for the various terms in a standard spherical harmonic expansion of the anisotropic two-body interaction. We have also clarified the role of SESO in promoting layer-thinning transitions in FSS films and we have proposed a novel mechanism that accounts for many aspects of the experimentally observed behavior.

Note added in proof. A recent experimental study indicates that the variation of FSS film tension with thickness during the thinning process for $T > T_{AI}$ is no greater than 1% [C. C. Huang, Phys. Rev. E (to be published)]. This finding constrasts sharply with the results of our model shown in Fig. 1, although it is to be recalled that the latter results do not correspond to layer-thinning transitions. The present theory predicts a considerably weaker variation of the film tension in the case corresponding to Fig. 3 (see [15]), and it is likely that with suitable model parameters the theory can reproduce film tension variaitons comparable to experimental results.

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[1] H. Kasten and G. Strobl, J. Chem. Phys. **103**, 6788 (1995).

[2] B. M. Ocko, A. Braslau, P. S. Pershan, J. Als-Nielsen, and M. Deutsch, Phys. Rev. Lett. **57**, 94 (1986); G. J. Kellogg, P. S. Pershan, E. H. Kawamoto, W. F. Foster, M. Deutsch, and B. M. Ocko, Phys. Rev. E **51**, 4709 (1995).

[3] P. S. Pershan, A. Braslau, A. H. Weiss, and J. Als-Nielsen, Phys. Rev. A **35**, 4800 (1987); P. S. Pershan, J. Phys. (Pans) Colloq. **50**, C7-1 (1989).

[4] Z. Pawlowska, T. J. Sluckin, and G. F. Kventsel, Phys. Rev. A **38**, 5342 (1988).

[5] J. V. Selinger and D. R. Nelson, Phys. Rev. A **37**, 1736 (1988).

[6] L. Mederos and D. E. Sullivan, Phys. Rev. A **46**, 7700 (1992).

[7] A. M. Somoza, L. Mederos, and D. E. Sullivan, Phys. Rev. Lett. **72**, 3674 (1994); Phys. Rev. E **52**, 5017 (1995).

[8] L. V. Mirantsev, Phys. Lett. A **205**, 412 (1995).

[9] C. Bahr, Int. J. Mod. Phys. B **8**, 3051 (1994).

[10] T. Stoebe, P. Mach, and C. C. Huang, Phys. Rev. Lett. **73**, 1384 (1994).

[11] 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 **53**, 3639 (1996).

[12] E. I. Demikhov, V. K. Dolganov, and K. P. Meletov, Phys. Rev. E **52**, R1285 (1995).

[13] B. Tjipto-Margo, A. K. Sen, L. Mederos, and D. E. Sullivan, Mol. Phys. **67**, 601 (1989).

[14] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon, Oxford, 1984), Vol. 1.

[15] Y. Martinez-Raton, A. M. Somoza, L. Mederos, and D. E. Sullivan, Faraday Discuss. (to be published).

[16] P. Pieranski *et al.*, Physica A **194**, 364 (1993).

[17] Y. Martinez, A. M. Somoza, L. Mederos, and D. E. Sullivan, Phys. Rev. E **53**, 2466 (1996).

[18] We note that the kinetics introduced in this way are by no means realistic. Local conservation of density, inhomogeneities in the xy directions, and boundary conditions are important in a realistic description. Nevertheless, we consider that this simple study provides qualitatively important information.

[19] The structure in Fig. 2(d) is similar to the ‘‘quasi-Sm-A’’ phase found by Mirantsev [8]. However, we disagree with the interpretation of Ref. [8] that such a film structure can be an intermediate stage in a layer-thinning transition. Instead, we believe that several fluctuation effects omitted from mean-field theory would lead to its spontaneous rupturing.

[20] S. Dietrich, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and J. L. Lebowitz (Academic, London, 1988), p. 1.