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Systematics of wetting and layering phenomena in smectic materials

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A lattice model is used to investigate the surface behavior of smectic fluids close to the onset of smectic ordering. At the smectic-isotropic interface the nematic features of the smectic phase persist further into the bulk isotropic phase than the strictly smectic features. At the isotropic-vapor interface we find the possibility of a series of first-order layering transitions, each involving the addition of a smectic layer, in line with recent experimental results. However, at the nematic-vapor interface surface smectic order, if it exists, grows smoothly without layering transitions.

I. INTRODUCTION

Wetting and capillary phenomena have long been studied by physicists and physical chemists.[1] A resurgence in interest in these phenomena took place about a decade ago[2] as it became clear that advances in experimental[3] and theoretical[4] techniques justified more detailed studies. Interest in surface phenomena in liquid crystals results partly from the importance of such phenomena in understanding liquid-crystal-based technological devices. After some initial studies,[5] it soon became clear that surface order in liquid crystals was a phenomenon related to the wetting properties of the liquid crystal in question.[6]

Wetting phenomena in nematics are of extra theoretical interest because not only is one concerned with the usual questions of the *quantity* of order at an interface, but also, as a result of the nature of the nematic order parameter, with the *direction* and *nature* of that ordering. This can lead to a variety of extra surface transitions, in addition to the familiar wetting and prewetting transitions.[7,8] Smectic liquid crystals show, in addition to the orientational order exhibited by nematics, positional order. In the smectic-*A* liquid crystals discussed in this paper, for example, there is layering perpendicular to the direction of nematic order.[9] Such systems might be expected to show a still richer pretransitional surface ordering before the onset of bulk order, including perhaps layering transitions, by analogy with multilayer growth of solids from a substrate.[10,11]

Recent experimental work on these systems has indeed produced interesting results. The first such study was by Rosenblatt and Amer[12] who studied freely suspended liquid-crystal films, and found that a number of liquid crystals undergo the nematic–smectic-*A* transition, for this geometry, at anomalously high temperatures. X-ray scattering from the free surface of nematic liquid crystals just above the nematic–smectic-*A* (*N*-*S*) transition showed the development of surface smectic order with the layering in the plane of the interface. This order persists in the bulk nematic for distances of the order of the bulk correlation length, a quantity which diverges at the (second-order) *N*-*S* transition. In addition an anomalous Gaussian-like decay in the smectic order has also been observed.[13] These results are consistent with other experimental results by Rosenblatt[14] who inferred, from anomalous Freidericksz transition phenomena in nematics confined in a thin sample between plates, the existence of surface smectic order close to a wall. The most dramatic manifestation of pretransitional smectic was obtained, however, by surface x-ray reflection from the liquid crystal decylcyanobiphenyl (12CB) which undergoes a direct isotropic-smectic phase transition. In these experiments a number of discrete layering transitions—as many as five—were observed for temperature just above the bulk phase transition, as the surface smectic order increased (but did not diverge).[15]

In this paper we make a theoretical analysis of pretransitional smectic surface phenomena in an attempt to interpret the experimental results mentioned above. The wetting paradigm is crucial in the interpretation of the theoretical results. We use a lattice model of smectic behavior introduced by Ronis and Rosenblatt,[16] which is itself a generalization of the model nematic now usually known as the Lebwohl-Lasher model.[17] Lattice models of complicated molecular systems such as liquid crystals are of course gross oversimplifications and one should be cautious about the extent of the their applicability. Nevertheless, bulk properties of nematic liquid crystals are well modeled using the Lebwohl-Lasher model,[18] and the bulk phase transitions of the model discussed in this paper correspond to known experimental features, as discussed in Sec. II. In addition powerful theoretical insight into wetting and layering phenomena in a more general context, although not perhaps quantitative agreement with experiment, has been obtained using lattice models.[10,11] A preliminary presentation of our results has already appeared.[19]

We draw the reader's attention to parallel work on the same subject by Selinger and Nelson.[20] These workers have used a density-functional theory to model the inhomogeneous fluid. Although in principle such a method should be superior to the kind of lattice model we discuss, there are in fact considerable problems in modeling even homogeneous smectic systems; the microscopic mechanisms responsible for the creation, and more importantly, the stabilization of the smectic-*A* phase, remain clouded in a certain amount of mystery.[21] We have attempted, nevertheless a brief comparison of the main conclusions of the respective studies.

The onset of smectic order may occur (a) by a first-order phase transition from the isotropic phase, (b) by a first-order phase transition from the nematic phase, or (c) by a continuous phase transition from the nematic phase. We find, for case (a) the possibility of a number of layering transitions, which are first-order apart from the very first—the onset of surface smectic order itself—which is continuous. In the models we examine however there is complete wetting (i.e., the number of layers diverges as the bulk phase transition approaches), in contradiction with the observed experimental results. In practice, however, only a few layering transitions are seen.[22] In cases (b) and (c), however, in contrast, we do not find layering transitions, but only the possibility of growth of the smectic surface region. This growth may diverge in case (b) and does diverge (if it exists at all) in case (c). We have not found the anomalous fall off of the smectic order parameter remarked upon for case (c) by the experimentalists,[13] although we do not find something resembling it for case (a).

A number of experiments have seen incommensurate[23] or antiferroelectric[24] surface order in addition to strictly pretransitional effects. We do not, however, address these phenomena in this paper.

The paper is organized in the following way. In Sec. II we setup the basic model, describe the method of solution and its bulk properties. In Sec. III we discuss the properties of liquid-liquid interfaces within the model—topics which have not thus far been the subject of experimental test. In Sec. IV we discuss the properties of the liquid-vapor (or more generally the liquid-wall) interface, concentrating on the induced surface order in the region just above the onset of smectic order [cases (a), (b), and (c) above], but starting with the rather well-understood surface setting properties of the Lebwohl-Lasher model to create the context in which to interpret the results. Finally in Sec. V we discuss our results and draw some conclusions.

II. MODEL

The Hamiltonian is defined on a simple cubic lattice. At each point i of the lattice there is a rotor whose direction $\hat{\mathbf{n}}_i$ is defined by Euler angles (θ,ϕ) and an (Ising) spin which takes values $\sigma_i=\pm 1$. In the tradition of lattice gas models σ_i corresponds to the local density ρ_i being greater than the average density $\bar{\rho}$. For some purposes it is useful to define the local nematic ordering tensor $Q_i^{\alpha\beta}=\frac{1}{2}(3\hat{\mathbf{n}}_i^{\alpha}\hat{\mathbf{n}}_i^{\beta}-\delta^{\alpha\beta})$, where the Greek superscripts correspond to Cartesian directions. The bulk Hamiltonian is

$$\mathcal{H}_0=-J\sum_{\{i,j\}}P_2(\cos\theta_{ij})+\epsilon\sum_{\{i,j\}}Q_i^{\alpha\beta}Q_j^{\alpha\gamma}(\hat{r}^{\beta}\hat{r}^{\gamma}-\tfrac{1}{3}\delta^{\beta\gamma})\sigma_i\sigma_j\ , \qquad (2.1)$$

where the sum is taken over pairs $\{i,j\}$ of nearest neighbors, and the unit vector $\hat{\mathbf{r}}$ joins the sites i and j. The parameter ϵ indicates the strength of the smectic interaction; $\epsilon=0$ corresponds to the (nematic) Lebwohl-Lasher model. This Hamiltonian is a subclass of the models introduced in Ref. 16.

The smectic part of the interaction (1) is such that if $\hat{\mathbf{r}}\cdot\hat{\mathbf{n}}=1$, it is antiferromagnetic, whereas if $\hat{\mathbf{r}}\cdot\hat{\mathbf{n}}=0$, it is ferromagnetic, although on average it is neutral. The first term induces nematic order for sufficiently low temperatures. The second term is essentially inactive in the high-temperature isotropic phase. However, when nematic order is established smectic order is possible, with σ taking opposite signs in alternate layers in a direction parallel to the nematic director, taken to be along one of the principal directions of the lattice.

We first discuss the bulk properties of this model. The nematic properties of a phase are described by the distribution function $f(\hat{\mathbf{n}})$ [$=(4\pi)^{-1}$ in the isotropic phase], and the nematic order parameter

$$Q=\bar{P}_2=\int P_2(\cos\theta)f(\hat{\mathbf{n}})d\hat{\mathbf{n}}\ . \qquad (2.2)$$

The smectic properties can be described by an order parameter $t=(-1)^m u; u=\bar{\sigma}$, where m is a layer index. The mean-field free-energy difference between the ordered and disordered phases per lattice site is given by

$$\Delta A=k_BT\int f(\hat{\mathbf{n}})\ln[4\pi f(\hat{\mathbf{n}})]d\hat{\mathbf{n}}+\frac{k_BT}{2}[(1+t)\ln(1+t)+(1-t)\ln(1-t)]-\tfrac{1}{2}(6JQ^2+2\epsilon Q^2t^2)\ , \qquad (2.3)$$

where k_B is Boltzmann's constant.

It is convenient to define $\tilde{T}=k_BT/6J$ and $\tilde{\epsilon}=\epsilon/6J$. The scaled free energy $\Delta\tilde{A}=\Delta A/6J$; henceforth all tildes are dropped. The equations which result from minimizing Eq. (2.3) are

$$Q=W[Q(1+2\epsilon t^2)/T]\ , \qquad (2.4a)$$

$$t=\tanh[2Q^2\epsilon t/T]\ , \qquad (2.4b)$$

where W is the Maier-Saupe function which occurs in the Maier-Saupe mean-field theory of liquid crystals.[25] This is the appropriate mean field theory for the Lebwohl-Lasher model.[17]

The resulting bulk phase diagram is shown in Fig. 1. This phase diagram has all the crucial features predicted in the early theory of smectic-*A* behavior by McMillan.[26] There are isotropic (*I*), nematic (*N*), and smectic (*S*) phases. For low ϵ there are three phases, with the *N*-*S* phase boundary continuous. However, beyond a tricritical point at $\epsilon=0.141$ this phase boundary becomes first order. The *N*-*S* transition line meets the usual first-order

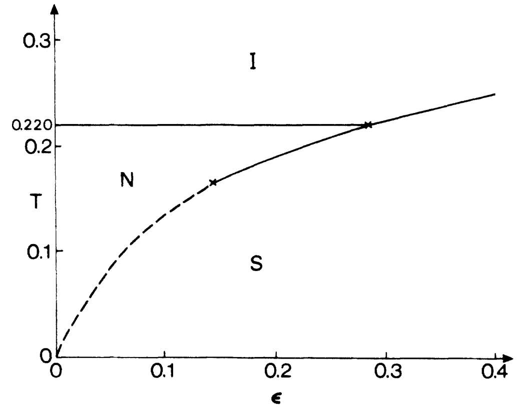

FIG. 1. Bulk phase diagram exhibiting isotropic (*I*), nematic (*N*), and smectic-*A* (*S*) phases. The *N*-*S* tricritical point is at $\epsilon=0.141$, $T=0.164$; the *N*-*S*-*I* triple point at $\epsilon=0.284$, $T=0.2202$.

N-*I* transition at $\epsilon=0.284$. Beyond this point the *N* phase is no longer stable, and there is a direct *S*-*I* transition, and T_{SI} increases with ϵ. In this regime there is strong order-parameter feedback. For instance, for $\epsilon=0$, $Q(T_{NI})\cong 0.42$, whereas at $\epsilon=0.3$, where many of our calculations are made, $Q(T_{SI})\cong 0.79$ and $t(T_{SI})\simeq 0.91$.

It is interesting to note that Thoen *et al.*[27] has drawn a similar phase diagram for the phases of the homogeneous series *n*CB, with the tail length *n* taking the place of the smecticity parameter ϵ. In this case the *S*-*N*-*I* triple point occurs at $n\approx 9.5$, $T_{\mathrm{tr}}\cong 318$ K. The experiments are carried out for $n=8$ and 12.[13,15]

Next we turn to inhomogeneous systems. Bulk system properties are given by Eq. (2.1). However close to a surface the effect of surface potentials comes into play. We are also concerned with boundaries between the phases given in Fig. 1. For semi-infinite systems, we take $m=1$ to be adjacent to the interface. The Hamiltonian is now

$$\mathcal{H}=\mathcal{H}_0-\sum_i V_i P_2(\cos\theta_i)-\sum_i H_i\sigma_i \ , \tag{2.5}$$

where V_i and H_i are surface potentials which are zero sufficiently far from the interface. The mean-field free energy per site in layer *m* is now given by the inhomogeneous extension of Eq. (2.3),

$$\Delta A_m = T\int f_m(\hat{\mathbf{n}})\ln[4\pi f_m(\hat{\mathbf{n}})]d\hat{\mathbf{n}}+\tfrac{1}{2}T[(1+t_m)\ln(1+t_m)+(1-t_m)\ln(1-t_m)]-\tfrac{1}{3}Q_m^2-\tfrac{1}{12}Q_mQ_{m+1}-\tfrac{1}{12}Q_mQ_{m-1}$$
$$-\epsilon(\tfrac{1}{2}t_m^2Q_m^2+\tfrac{1}{4}t_mt_{m+1}Q_mQ_{m+1}+\tfrac{1}{4}t_mt_{m-1}Q_mQ_{m-1})-V_mQ_m-(-1)^mH_mt_m \ . \tag{2.6}$$

Minimizing the total free energy

$$\Delta A=\sum_m \Delta A_m \tag{2.7}$$

yields the following mean-field equations:

$$Q_m=W(x_m)\ , \tag{2.8a}$$

where

$$x_m=\frac{1}{T}[\tfrac{2}{3}Q_m+\epsilon t_m^2Q_m+\tfrac{1}{6}(Q_{m-1}+Q_{m+1})+\tfrac{1}{2}\epsilon t_m(t_{m+1}Q_{m+1}+t_{m-1}Q_{m-1})+V_m]\ , \tag{2.8b}$$

$$t_m=\tanh y_m\ , \tag{2.9a}$$

where

$$y_m=\frac{\epsilon Q_m}{T}[Q_mt_m+\tfrac{1}{2}(Q_{m+1}t_{m+1}+Q_{m-1}t_{m-1})]+\frac{K_m}{T} \tag{2.9b}$$

and

$$K_m=(-1)^mH_m\ . \tag{2.9c}$$

We remark that Tx_m and Ty_m are, respectively, the mean fields felt by the order parameter Q_m and t_m.

The equations [(2.8) and (2.9)] are solved iteratively using the procedure

$$Q_m^{(n+1)}=W(x_m^{(n)})\ , \tag{2.10a}$$

$$t_m^{(n+1)}=\tanh y_m^{(n)}\ , \tag{2.10b}$$

where the superscripts are iteration indices. The quantities $x_m^{(n)}, y_m^{(n)}$ are related to $Q_m^{(n)}$, $t_m^{(n)}$ using Eqs. (2.8b) and (2.9b). In some cases there is more than one stable solution. When discussing interphase boundaries or adsorption effects it is important that the system size be sufficiently larger than the length scale of the phenomenon under examination, and in some cases the stability of particular solutions was tested under system size change. Most of our calculations were for systems of between 20 and 50 layers.

Finally we note that, from a formal point of view, one smectic layer corresponds to two layers in our system. However, apart from convention, there is nothing obligatory in the mapping $\sigma>0$ corresponding to the above average density. An opposite choice would have been equally consistent. This will have some consequences in our discussion of semi-infinite systems, and in particular with respect to "free" surfaces in which for a full self-consistent treatment it would be necessary to consider density variations in the immediate liquid-vapor interface region. We shall return to this point later in the paper. In all our discussions, however, we consider the behavior of the order parameter *t* (rather than *u*); this is the envelope of the amplitude of the density oscillations.

III. LIQUID-LIQUID INTERFACES

We do not discuss here the nematic-isotropic ($N-I$) interface which occurs for $0 \leq t < 0.284$ and which has been much discussed elsewhere[18] other than to remark that in our model the surface free energy per unit area $\gamma_{NI} = 0.00385$ and the 10-90 width of the surface region is 5.7 lattice units. This width, which is the distance over which the middle 80% of the order-parameter change in the interface takes place, is traditionally used as a measure of interface thickness. These quantities serve as markers for the magnitudes of quantities in other calculations.

We now discuss the smectic-isotropic (*S-I*) interface which occurs for $\epsilon \geq 0.284$. We first make an asymptotic analysis far into the isotropic phase; we shall suppose that the layer index $m \rightarrow -\infty, +\infty$ in the *S*, *I* phases respectively. In this regime the order parameters Q_m, t_m and the mean fields x_m, y_m are small; there are not externally applied fields. In this limit Eqs. (2.8) and (2.9) reduce to

$$Q_m = \frac{1}{5T}\left(\tfrac{2}{3}Q_m + \tfrac{1}{6}Q_{m+1} + \tfrac{1}{6}Q_{m-1}\right) , \tag{3.1}$$

$$t_m = \frac{\epsilon}{T} Q_m\left(Q_m t_m + \tfrac{1}{2}Q_{m+1}t_{m+1} + \tfrac{1}{2}Q_{m-1}t_{m-1}\right) . \tag{3.2}$$

The factor $\frac{1}{5}$ arises because $(\partial W/\partial x)(0) = \frac{1}{5}$.[25]

A standard analysis now yields

$$Q_m \sim e^{-\kappa m} , \tag{3.3}$$

where

$$e^{-\kappa} = 3\left[1 - \frac{2}{15T}\right] - \left[9\left[1 - \frac{2}{15T}\right] - 1\right]^{1/2} . \tag{3.4}$$

The behavior of t_m is rather different, however, as a result of the nonlinear couplings. In Eq. (3.2) the last term dominates in the asymptotic limit, and now

$$t_m \sim e^{-\kappa m^2} . \tag{3.5}$$

The decay of t_m is much more rapid than that of Q_m and this suggests that the nematic features of the smectic phase persist much further into the isotropic phase near the *S-I* interface than the strictly smectic features. These conjectures are borne out by explicit calculation. In Fig. 2 we show the normalized order-parameter profiles at the *S-I* interface for $\epsilon = 0.3$. The 10-90 width of the Q profile is 5.3 lattice units; this is slightly less than the *N-I* profile, but can be accounted for by the increase in the value of Q_s as compared to Q_N. By contrast, the 10-90 width of the t profile is only 2.5 lattice units. In addition the median point of the t profile (the point where $t/t_{\text{bulk}} = 0.5$) is shifted in the direction of the smectic phase by 1.5 lattice units as compared to the median point of the Q profile. The dramatic difference between the S and I phases is highlighted by the value of $\gamma_{SI} \cong 0.036$; a factor of 10 larger than the surface free energy at the *NI* interface.

This phenomenon is even more evident in Fig. 3 which shows the *S-I* interface at $\epsilon = 0.284$ just beyond the *S-N-I* triple point in the region of direct *S-I* coexistence. In this case the t profile is essentially unchanged, but the Q profile has broadened to 10.4 lattice units, and the shift between the medians has increase to five lattice units. The crucial point about this profile, however, is the development of the shoulder in the Q profile, which appears to be diverging as the triple point is approached. This shoulder is the signature of the metastable nematic phase coexisting with the *S-I* phases; the N phase is here seen *wetting* the *S-I* interface.[28] In the limit of the triple point we expect here a macroscopically thick N phase interposed between the S and I phases, with $Q_N/Q_S = 0.42/0.79 \cong 0.53$. We see in Fig. 3 that the flat region indeed occurs for $Q/Q_s \approx 0.53$.

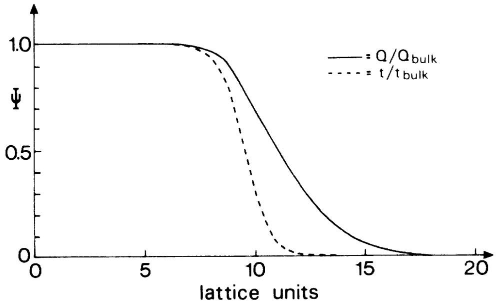

FIG. 2. The *S-I* interface at $\epsilon = 0.3$. Normalized order parameter Ψ is plotted against distance (in lattice units).

We turn now to the smectic-nematic (*S-N*) interface which occurs between the *S-N* tricritical point at $\epsilon = 0.141$ and the *S-N-I* triple point at $\epsilon = 0.284$. We make an asymptotic analysis in the region far into the nematic phase, by taking the limiting cases of Eqs. (2.8) and (2.9). We obtain

$$\delta Q_m = \frac{1}{T}\frac{\partial W}{\partial x}(x_N)\left(\tfrac{2}{3}\delta Q_m + \tfrac{1}{6}\delta Q_{m+1} + \tfrac{1}{6}\delta Q_{m-1}\right) , \tag{3.6}$$

$$t_m = \frac{\epsilon Q_N^2}{T_{NS}}\left(t_m + \tfrac{1}{2}t_{m+1} + \tfrac{1}{2}t_{m-1}\right), \tag{3.7}$$

where $Q_m = Q_N + \delta Q_m$. Q_N is the equilibrium value of the nematic order parameter in the N phase, and

$$Q_N = W(x_N) .$$

One now obtains

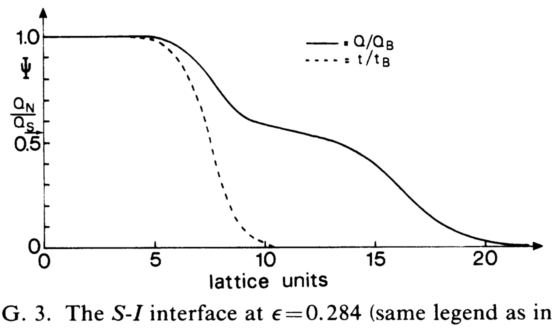

FIG. 3. The *S-I* interface at $\epsilon = 0.284$ (same legend as in Fig. 2). The nematic order parameter has developed a shoulder indicating perfect wetting of this interface by the N phase.

$$\delta Q_m \sim e^{-\kappa_1 m}, \text{ where } e^{-\kappa_1} = 3(1-\tfrac{2}{3}\lambda) - [9(1-\tfrac{2}{3}\lambda)^2 - 1]^{1/2} \tag{3.8}$$

and

$$\lambda = \frac{1}{T}\frac{\partial W}{\partial x}(x_N) ;$$

whereas

$$t_m \sim e^{-\kappa_2 m} \tag{3.9}$$

with

$$\mathrm{sech}^2 \frac{K_2}{2} = Q_N^2 \epsilon / T_{NS} . \tag{3.10}$$

A particularly interesting limit is close to the tricritical point. At the tricritical point, from Eq. (2.4),

$$\frac{Q_N^2 \epsilon}{T_{NS}} = \frac{1}{2} , \tag{3.11}$$

and thus the distance from the tricritical point can be parametrized by a parameter δ, where

$$\frac{2Q_N^2 \epsilon}{T_{NS}} = 1 - \delta . \tag{3.12}$$

Comparison of Eqs. (3.10) and (3.12) in the limit $\delta \rightarrow 0$ now yields

$$\kappa_2 \sim 2\delta^{1/2} . \tag{3.13}$$

The lengths $l_1 = \kappa_1^{-1}$, $l_2 = \kappa_2^{-1}$ are the relaxation lengths for nematic and smectic perturbations, respectively. The relaxation length for smectic perturbations becomes large at the *N-S* phase transition, and diverges at the tricritical point (and indeed all along the second order *N-S* line $\epsilon < 0.141$).

This asymptotic analysis suggests that the *N-S* interface, in contrast to the *S-I* interface, it is the *t* profile which is broader than the *Q* profile, and that the center of the *t* profile will be shifted in the direction to the *N* phase, as compared to the center of the *Q* profile.

More detailed calculations confirm these general remarks. We show an example in Fig. 4, in which for $\epsilon = 0.2$, the profile medians are separated by roughly 0.7 lattice units. We note, however, that as a result of the (nonlinear) coupling between the *Q* and *t* profiles, both profiles diverge as the tricritical point is approached.

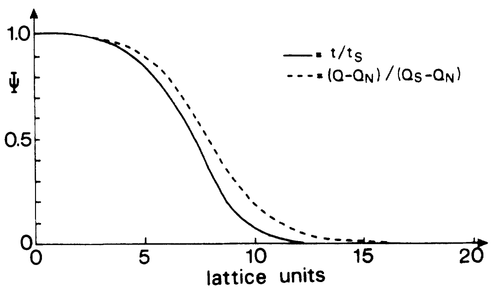

FIG. 4. The *S-N* interface at $\epsilon = 0.2$. Solid line, $(Q - Q_N)/(Q_S - Q_N)$; dashed line, t/t_S.

We now make some more general comments about the applicability of the results of this section. The most striking feature of the *S-I* interface is the Gaussian, rather than exponential, fall off of the *t* profile in the asymptotic *I* limit. This is surely, however, an artifact of the model, and results because there is no direct nearest-neighbor *t* interaction in the Hamiltonian. It seems likely that a more realistic model would replace the Gaussian by a rapid exponential decay. The corollary of this result, however—the increased width of the *Q* profile and its shift relative to the *t* profile—seem much more stable and result from the general physics that lie behind the model rather than the details of the Hamiltonian. In the *S-N* profile we found that it is the *t* profile which is thicker, in contrast to the *S-I* case. In the asymptotic analysis, Eqs. (3.6) and (3.7), the *Q* and *t* decays correspond to different eigenvalues; an improved model would probably mix these decays, but we speculate nevertheless that the result concerning the relative position of the profile media and their relative thickness would still hold. There is a final corollary. In most of the work in Sec. IV there is some tendency for formation of smectic layers at an imposed surface. Associated with the smectic surface order is surface nematic order. The considerations of this section suggest that if the bulk is *isotropic*, there is in some sense (defined more precisely in Sec. IV) more nematic than smectic order at the interface, whereas by contrast if the bulk phase is *nematic*, the reverse applies.

IV. THE FREE SURFACE

We model the free surface by taking a semi-infinite system with layers $m = 1 - \infty$, subject to the Hamiltonian (2.5). We take a surface potential

$$\mathcal{H}_S = -VP_2(\cos\theta_1) \tag{4.1}$$

acting on the first layer only. This term, as in a number of physical situations, acts as a surface anchoring term on the nematic director close to the interface. All ordering effects at the free surface follow from this term. The surface ordering competes with the lack of nearest neighbors close to the interface. Through the interaction with the smectic order parameter it can in principle induce, as well, smectic order close to the interface.

The theory is not self-consistent in the sense that the theory does not exhibit, as of itself, a vapor phase in equilibrium with the liquid phases. The approach we adopt is nevertheless likely to be successful so long as the liquid-vapor interface is thin on the scale of other length scales in the system. Liquid-crystal phases are in general far from liquid-vapor critical points and this assumption is in general correct.

We shall find it useful to define the surface free energies, defined per unit area, associated with the free surface γ_I, γ_N, γ_S, applicable, respectively, in the isotropic, nematic, and smectic phases. The interface free energies at the *S-I* and *S-N* interfaces are then γ_{SI} and γ_{SN}.

The precise value of *V* appropriate to the liquid-vapor interface is not known. We shall therefore study the properties of interface as a function of *V*. The surface potential can also be tuned by considering semi-infinite systems close to a wall at which homeotropic boundary conditions are applied.

In the remainder of this section we consider a number of cases in turn. We first discuss the growth of nematic order for the $\epsilon=0$ case above $T=T_{NI}$. We then discuss the case of surface smectic order for the direct *S-I* transition, and then discuss surface smectic order for the *S-N* transitions; in the last case the first- and second-order *S-N* transitions exhibit slightly different behavior.

A. Surface nematic order

The growth of nematic wetting layers has now been much discussed in the literature.[6] In this section we merely present a number of results which are qualitatively already known, but which serve as orientation for the surface smectic order studies.

Surface order is measured by the quantity

$$\Gamma(Q)=\sum_{m=1}^{\infty} Q_m/Q_N(T_{NI}) . \tag{4.2}$$

This gives, using the Gibbs criterion, the number of surface nematic layers.

We present results for $\epsilon=0$ (the mean-field theory is the same for all $\epsilon<0.284$) and $T\geq T_{NI}=0.220\,19$. For $V=0$, as found earlier[18] there is complete wetting of the surface by the isotropic phase. For $V>0$ there is partial wetting of the interface, and at $V=V_w=0.07$ there is a *second-order* wetting transition. For $V>V_w$ the nematic phase wets the surface; equivalently $\Gamma(Q)$ diverges in this regime. As expected in theories of this type, in the region close to V_w along the line $T=T_{NI}$, we find $\Gamma(Q)\sim\ln(V_w-V)$, and once in the wetting regime $\Gamma(Q)\sim\ln(T-T_{NI})$.

B. Surface smectic order close to the *S-I* transition

Our calculations are carried out for $\epsilon=0.3$. The relevant surface "adsorptions" are now

$$\Gamma(Q)=\sum_{m=1} Q_m/Q_s(T_{SI}) , \tag{4.3a}$$

$$\Gamma(t)=\sum_{m=1} t_m/t_S(T_{SI}) , \tag{4.3b}$$

where $\Gamma(Q)$ and $\Gamma(t)$, as above, give measures of the number of adsorbed layers using, respectively, the Gibbs criterion on the nematic and smectic order parameters.

As an example of the kind of results we obtain we show in Fig. 5 a plot of $\Gamma(Q)$ and $\Gamma(t)$ as a function of temperature above T_{SI}, for $V=0.8$. The relevant scale is logarithmic. A number of features are noticeable in this plot. $\Gamma(Q)$ is consistently larger than $\Gamma(t)$, with $\Gamma(Q)-\Gamma(t)\sim 2$. This was already predicted qualitatively at the end of Sec. III; it is the signature of the emergence of an embryonic "smectic-isotropic" interface between the surface smectic order close to the surface and the bulk isotropic phase. Feature *A* corresponds to the onset of surface smectic order. This is a *continuous* surface phase transition, occurring at T_{ss}, and near which, as far as we can tell, $\Gamma(t)\sim(T_{ss}-T)$. Features *D*, *E*, and *F* are layering transitions between, respectively, 3 and 4, 4 and 5, and 5 and 6 surface smectic layers. These transitions are *first order.* Features *B* and *C* are anomalies in the adsorption isotherm which correspond to the transitions between 1 and 2, and 2 and 3 surface smectic layers. They are strongly reminiscent of pretransitional layering phenomena. They are not phase transitions in the thermodynamic sense. Their existence suggests, however, that for slightly different thermodynamic control parameters first-order surface phase transitions between 1 and 2, and 2 and 3 layers, also exist.

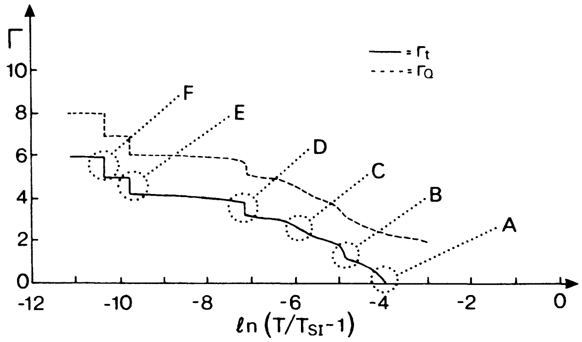

FIG. 5. Layer growth above T_{SI} for $\epsilon=0.3$, $V=0.8$. Solid line, $\Gamma(t)$; dashed line, $\Gamma(Q)$. Features *A*–*F* (marked) are discussed in the text.

All features in $\Gamma(t)$ are mirrored in $\Gamma(Q)$, apart from the initial onset of surface smectic behavior. Very close to the phase transition there are also metastable states with $\Gamma(t)=7$, 8, 9, etc. In this region it becomes difficult to distinguish numerically between the stability of the various solutions. It is not *a priori* clear whether the hierarchy of layering transitions continues to $\Gamma(t)=\infty$ (i.e., perfect wetting of the surface by the smectic phase) or terminates at $\Gamma(t)=6$, as shown in Fig. 5 (i.e., partial wetting by the smectic phase). This question can, however, be answered by studies over a variety of *V*. In Fig. 6 we show the behavior of the contact angle θ at the *S-I* vapor contact line where θ is defined in the usual way,[4,6] using the Young-Laplace formula

$$\gamma_s-\gamma_I=\gamma_{SI}\cos\theta . \tag{4.4}$$

This plot shows that there is a wetting transition at $V=0.645$, beyond which a macroscopic smectic layer interposes itself between the isotropic phase and the sur-

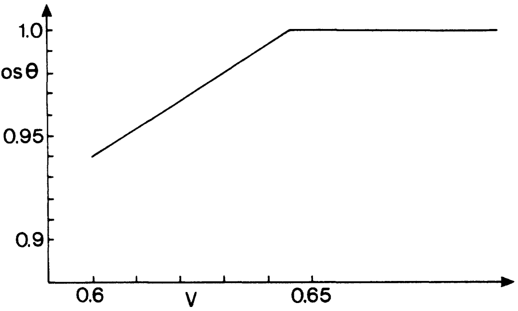

FIG. 6. Contact angle $\cos\theta$ plotted against surface potential *V* for $\epsilon=0.3$ at T_{SI}, indicating a wetting transition at $V=0.645$.

face. The linear behavior of $\cos\theta$ in the region $V < 0.645$ establishes that the transition is first order.[4] We are not, of course, able to observe the growth of an infinite layer, in a finite system. The existence of a first-order wetting-like transition convinces us nevertheless that in an infinite system this is what we would see.

In Fig. 7 we exhibit a wetting-layering surface phase diagram, as a function of V and T. This shows the *first-order* wetting transition at $V_w = 0.645$, the continuous surface smectic transition line, the layering transitions, and critical points at which the 1-2 and 2-3 layering transitions end. However, the detail of the higher layering transitions very close to T_{SI} is not visible on the scale of this diagram.

An interesting point to note is that the wetting transition occurs for a value of $V = 0.645$, which is much larger than necessary for wetting the $\epsilon = 0$ interface with N phase ($V_w = 0.07$). We ascribe this primarily to the increased order parameters in the ordered phase, which require larger surface forces to maintain them in the bulk I phase.

C. Surface smectic order above the first-order S-N transition

Our calculations are carried out for $\epsilon = 0.2$, for which $T_{SN} = 0.190\,115$. Here, in contrast to the previous case, we do not find layering transitions, although we do find induced surface order.

The relevant adsorption parameters are now

$$\Gamma(Q) = \sum_{m=1}^{\infty} [Q_m - Q_N(T_{SN})]/[Q_s(T_{SN}) - Q_N(T_{SN})] , \tag{4.5a}$$

$$\Gamma(t) = \sum_{m=1}^{\infty} t_m / t_S(T_{SN}) . \tag{4.5b}$$

As an example of the growth of surface order we show in Fig. 8 the growth of $\Gamma(t)$ for $V = 1.2$. It is logarithmic as a function of $(T - T_{SN})$ over more than 3 orders of magnitude. We thus have a divergence of $\Gamma(t)$ close to T_{SN}, and complete wetting of the surface by the smectic phase. The full surface phase diagram as a function of V and T is shown in Fig. 9. This is a much simpler version of the previous surface phase diagram of Fig. 7. The continuous surface smectic transition line remains, but now a *continuous* wetting transition to complete smectic film growth occurs at $V_m = 1.1$, much higher than the onset of surface smecticity at T_{SI}, at $V_{SS}(T_{SI}) = 0.57$.

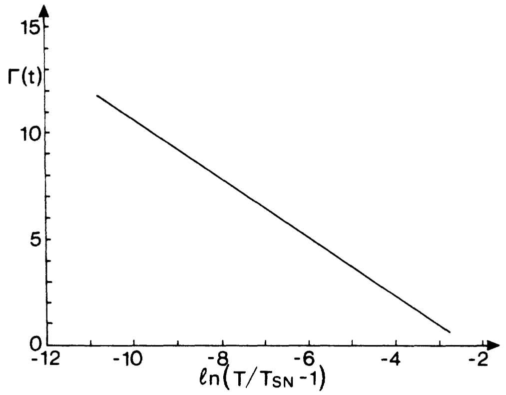

FIG. 8. The growth of smectic order from the nematic phase at $\epsilon = 0.2$, $V = 1.2$. The logarithmic dependence of $\Gamma(t)$ is characteristic of complete wetting. Note the absence of layering transitions.

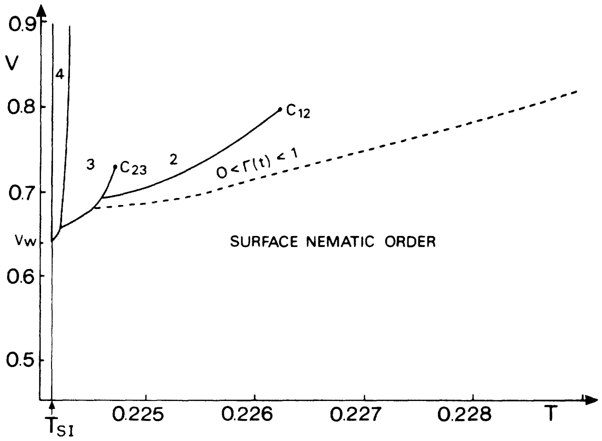

FIG. 7. Surface wetting-layering phase diagram for $\epsilon = 0.3$. Solid lines are (first-order) layering transitions, terminating at the critical points C_{12} and C_{23}. The dashed line marks the (continuous) onset of smectic order. Numbers indicate the number of smectic layers.

D. Surface smectic order above the continuous S-N transition

We present here a typical calculation, at $\epsilon = 0.1$, for which $T_{SN} = 0.135\,083$. The crucial difference as compared to the previous example is that now the susceptibility to smectic layer formation diverges at the continuous S-N transition. The concept of a wetting layer is no

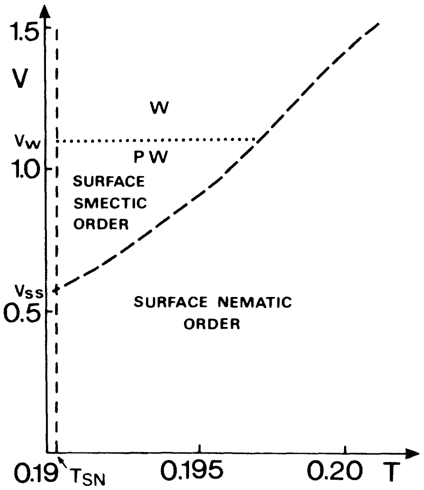

FIG. 9. Surface phase diagram for $\epsilon = 0.2$. Note that the dashed line marks the (continuous) onset of surface smectic order. The dotted line highlights the wetting transition at V_w between complete wetting (W) and partial wetting (PW) regimes.

longer useful. The divergence in correlation lengths makes calculations of analogues of $\Gamma(t)$ somewhat difficult close to the transition. In any case, if there is surface order such quantities diverge at T_{SN}. We show the surface phase diagram in Fig. 10. As compared to the previous example it has of course lost the wetting transition, but the continuous surface smectic transition remains. The best measure of the quantity of surface order is given by the surface order parameter t_1. In the region of the phase diagram shown, this reaches ~ 0.2.

We remark on the analogy between the surface phase diagram exhibited here, and the surface phase diagram which can occur in magnetic systems close to the second-order Curie points.[29] In this magnetic language for $V < V_{SS}(T_{SI}) = 1.72$ the surface exhibits an *ordinary* transition, for $V > V_{SS}(T_{SI})$ the onset of surface smectic order is an *extraordinary* transition, and at $V = V_{SS}(T_{SI})$ there is a *special surface* transition.

V. DISCUSSION AND CONCLUSIONS

In our discussion we concentrate on the results of Sec. IV which represent our modeling of the free interface of a liquid just above a liquid-crystal transitions. The most striking results are the layering transitions just above the *S-I* transition (Fig. 5) and the consequent wetting-layering surface phase diagram (Fig. 7). These results correspond to 12CB, studied by Ocko *et al.* and Als-Nielsen[15].

In our preliminary calculation we failed to observe these layering transitions, partly because there is only weak hysteresis involved up to $\Gamma(t) = 4$, whereas the higher layering transitions are subject to very strong hysteresis effects; technically speaking it was necessary to search for the $\Gamma(t) = 5$, 6, etc., solutions. The "quasiwetting" we referred to, was metastable $\Gamma(t) = 4$ solution, which has an energy very close to a complete wetting solution. It is now clear that this was an artifact.

Our present, more complete, study shows $\Gamma(t) = 5$, 6, 7 solutions which are thermodynamically stable, as well as $\Gamma(t) = n > 7$ solutions which are indistinguishable in energy at $T = T_{SI}$ on the accuracy which is available to us. From the circumstantial evidence of the contact angle (Fig. 6), we infer that there is in fact infinite (though presumably discontinuous) layer growth, but this is unlikely to be observable on a sensible temperature scale. The actual *size* of this wetting layer is, however, much smaller than the *S* wetting layer growing from the *N* phase (Fig. 8), or the *N* wetting layer growing from the *I* phase, discussed in Sec. IV A but not shown.

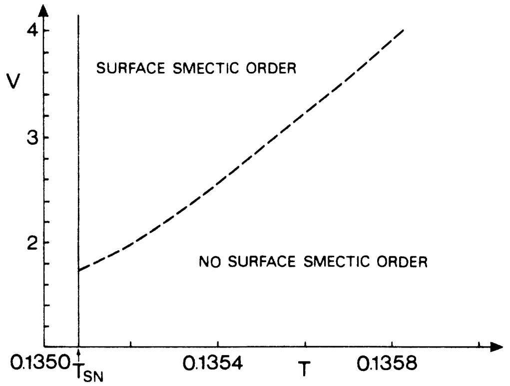

FIG. 10. Surface phase diagram at $\epsilon = 0.1$. All that remains of the menagerie of transitions in Fig. 7 is the dashed line marking the onset of surface smectic order.

A particular feature of our results is the growth of "half-integer" smectic layers (recall the 1 smectic layer = 2 lattice layers). This is clearly an artifact of our model. A more realistic model would include the mean density as a separate variable, and would essentially choose, say, the $\Gamma(t) =$ even solutions as opposed to the $\Gamma(t) =$ odd solutions. It is less clear how to introduce such a correction into our model, and there is some doubt as to how useful this exercise would be in the context of a study such as ours. In our previous paper[10] we accomplished this by introducing a long-range force which coupled with the density field. This choice is between odd and even $\Gamma(t)$ solutions, but only at the price of eliminating the surface smectic transition; some smectic order is now always present.

But there are many studies in normal liquids to show that, despite early speculations by Croxton,[30] there is in general no surface smectic order in fluids. The real problem is that in our model the surface is localized ("smooth" in the language of the roughening transition), whereas a real fluid has a delocalized, "rough" surface. This delocalization is sufficient to smear out any density fluctuations near the surface, unless there are other physical forces (such as discussed in this paper) to the contrary. The input of a surface field coupling to the density and the delocalization of the surface have opposite effects, leaving a qualitatively correct phase diagram, but with "too many" layering transitions.

In all cases at the onset of surface smectic order we find $\Gamma(t) \sim \Delta T = T_{SS} - T$. This result seems slightly surprising in the context of mean-field theory; normally the onset of an order parameter at a second-order phase transition might be expected to show $\Gamma(t) \sim \Delta T^{1/2}$ in accordance with Landau theories. Our result is numerical, however. More detailed experimental work in this regime is clearly desirable.

In our first letter we invoked the mechanism of de Olivera and Griffiths[11] to explain, qualitatively, the layering phenomena. In this mechanism there is a long-ranged surface field and a bulk field which compete. In that picture layering resulted from competition between forces of different ranges. It is clear from the present calculations that this mechanism was not necessary; in this paper we obtain layering with only local surface forces. We find this somewhat surprising; it presumably arises from the nonlinearity of the model.

A striking feature of our results is that *either* we find a series of layering transitions which appear to lead to complete wetting by the smectic phase, *or* we have no smectic surface order whatsoever. It is difficult to know, *a priori,* how much universality to apply to this result. Why do we not find a series of layering transitions leading to partial wetting? This does not appear to be forbidden by any theorem. It may be that an even more careful study would give rise to this possibility too. The experiments on 12CB free surfaces seem to show layering and partial wetting by the smectic phase, as does the density functional theory of Selinger and Nelson.[20] Nevertheless the similarity between the general features of our results (Fig. 7) and the experiments[15] is somewhat persuasive; it may be simply that further layering transitions would involve probing a temperature scale too fine for present experimental techniques. In any event measurements of the surface tensions γ_S, γ_I, and γ_{SI} would presumably resolve this question.

Another interesting contrast is between the layering transitions leading to growth of the smectic phase at the I free surface at T_{SI}, on the one hand, and the smooth growth of the smectic surface layer (Fig. 8) at the N free surface at T_{SN}, on the other. Once again there does not appear to be a theorem enforcing this, but it seems to be consistent with the available experimental results;[13] there, in contrast again with the results close to T_{SI}, there does appear to be a possibility of growth of a smectic layer to partial wetting. We note, in passing, the similarity from a theoretical point of view, between the continuous surface smectic transition discussed here, and the surface symmetry breaking transition predicted by one of us[7,8] in nematics close to a surface with tangential boundary conditions. The analogy between this transition and similar transitions in magnets for the case when the S-N transitions is second order has already been remarked upon. We emphasize that this case tends to be the experimentally observed case, as in 80CB.[13]

Finally we make a few comments about the density-functional theory of the same phenomena by Selinger and Nelson.[20] They remark that it is possible that a lattice theory would be unreliable and give rise to spurious layering transitions. We cannot, of course, rule this out. Nevertheless we note that our theory makes strikingly different predictions about layer growth for a free I surface above T_{NI}, a free I surface above T_{SI}, and a free N surface above T_{SN}, and that qualitatively speaking these predictions are borne out by experiment. Selinger and Nelson found fewer layering transitions than we did in the case of growth of smetic layers close to the I surface, and found always partial wetting in these cases. An experimental study of the wetting behavior at this surface using other techniques is clearly required. They speculate that the reason that they find fewer layering transitions than the experiments is that mean-field theories fail to take into account fluctuations which lower the bulk phase transition, thus leaving, as it were, more space for surface layering transitions to manifest themselves. We are skeptical of this argument; our model provides the required number of layering transitions, is a mean-field theory, and because it is a lattice model, is less susceptible to fluctuation effects. However, what is clear is that a full self-consistent density functional theory with general potentials and allowing for the existence of vapor, isotropic liquid, and liquid-crystal phases would be expected to yield more detailed results than our theory can hope to do.

In conclusion we have provided a framework, using a rather unsophisticated lattice model, and a rather unsophisticated mean-field theory of the model, which enables the behavior of smectic-forming materials near a free interface, in particular just above the onset of smectic behavior, to be understood. Rather good qualitative agreement with experiment results has been obtained. The record of such theories, despite their lack of sophistication, is rather good, and there seems some ground for hoping that the agreement with experiment might even be made quantitative in the future. The theory, however, is really applicable to *any* interface, and we strongly suggest experiments on smectic pretransitional effects on treated surfaces, by analogy with successful experiments on nematic pretransitional behavior.[5]

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