

Unified model of the smectic-*A*, nematic, and isotropic phases for bulk, interfaces, and thin films. II. Interfaces and thin films

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Using material parameters determined by bulk behavior, and the lattice model presented previously by us [Phys. Rev. A **21**, 1687 (1980)], we study interfacial and thin-film phenomena in the mean-field approximation. The effects of free and solid surfaces on orientational ordering for the isotropic phase are found to depend on the details of the intermolecular interaction and, sufficiently far above the supercooling limit, the decay length is on the order of a molecular dimension. For some materials, we find smecticlike thin films at temperatures above the bulk nematic-isotropic transition, enhanced orientational ordering, and the possibility of multiple smecticlike phases.

I. INTRODUCTION

In recent years there has been a growing interest in the behavior of liquid crystals (LC) at a nonliquid crystal (particular air or glass) interface. Langevin¹ and Langevin and Bouchiat² have measured surface tension and viscosity coefficients at a LC-air interface in the nematic and smectic-*A* phases. One of the viscoelastic coefficients was observed to diverge at T_{NS} and its exponent to be consistent with mean-field behavior. Using a Landau-de Gennes model, Sheng³ has investigated the nematic-isotropic (NI) transition in thin samples with one free surface. In particular, he showed that for sufficiently thin samples, the NI transition can become second order, unlike the bulk first-order transition. Other workers⁴⁻⁶ have investigated systems of freely-suspended thick nematic films, measuring director orientation and electrohydrodynamic behavior.

Of practical interest is the study of a LC-glass interface, particularly in light of current efforts in display technology. Miyano⁷ has studied the effects of a LC-glass interface on the orientational order parameter of a bulk isotropic material. He noted strong ordering at the treated glass surface which decays to zero in the bulk with some characteristic length. This analysis, utilizing a Landau-de Gennes model, successfully explained his experimental results. Recently, Akahane and Tako⁸ have presented a Maier-Saupe model, valid far from T_{NI} , for nematic order between treated substrates. Other effects, such as local biaxiality near a (LC-non-LC) interface, have also been investigated. Naggiar⁹ using para-azoxyanisole (PAA) and Bouchiat and Langevin-Cruchon¹⁰ using methyl-oxybenzylidene butylaniline (MBBA) have observed that the director is tilted by some angle Θ with re-

spect to the surface normal near a LC-air interface. In an attempt to explain this phenomenon, Parsons¹¹ has presented a Landau model utilizing competing van der Waals and dipolar forces. Finally, Mada^{12,13} has recently presented a model for the analogous behavior at a LC-glass interface.

In addition to interfacial and thick-film phenomena, several workers¹⁴⁻¹⁸ have recently investigated very thin freely suspended smectic films. These films, quantized in thickness, have been made as thin as one smectic layer¹⁶ and have been used to study surface orientation and nonlocal effects,¹⁵ as well as two-dimensional phase transitions^{16,18} such as those proposed by Kosterlitz and Thouless¹⁹ and Halperin and Nelson.²⁰ Rosenblatt and Amer have also shown¹⁷ that the smectic-*A* phase in thin films can exist at anomalously high temperatures and that the orientational order parameter can differ from corresponding bulk values in these films.

Until recently many of these phenomena have been treated theoretically in an isolated framework. To date no Hamiltonian theory has been successful in explaining surface and bulk behavior in a way that avoids the necessity of introducing new surface parameters.

In this work, we apply our lattice model²¹ (in the mean-field approximation) to the study of very thin films and the effects of free and solid surfaces on the various order parameters. Unlike the earlier approaches, the material parameters appearing in this work are the same used in the study of the bulk phases.

The paper is divided into five sections, of which this is the first. In Sec. II we review the essential features of the model, particularly as applied to bulk. Thin films with two free surfaces are covered in Sec. III. In Sec. IV we apply the model

to a LC-air interface and demonstrate the possibility of surface-induced orientational order. Finally, in Sec. V we present a critical discussion of the model, its successes and failures, and suggest ways of improving the theory.

II. REVIEW OF THE MODEL

In our earlier paper²¹ (hereafter referred to as "I"), we presented a lattice model for the smectic-A, nematic, and isotropic phases in bulk. A cubic lattice was introduced in which the cell spacing was $d/2$ along the preferred (\hat{z}) axis, where d is the smectic layer spacing. Two-cell periodicity was assumed along \hat{z} , and translational invariance was assumed in the $\hat{x}\hat{y}$ plane. A given cell can have occupation 0 or 1, where the chemical potential is set such that the total number of particles N is specified; N is normally one particle per pair of cells for the bulk. In addition, associated with each of the two cells is an orientational order parameter

$$s_i = \langle n_i P_2(\cos \theta_i) \rangle.$$

(The angular brackets denote an equilibrium average.)

We first assumed that pairs of molecules with orientation vectors $\vec{\Omega}_i$ and $\vec{\Omega}_j$ have an interaction of the form

$$\begin{aligned} U_{ij}(\vec{\Omega}_i, \vec{\Omega}_j) = & \epsilon_{ij} + \xi_{ij} \hat{r}_{ij} \hat{r}_{ij} : [\underline{T}_i + \underline{T}_j] \\ & + J_{ij} (\underline{T}_i : \underline{T}_j + G_{ij}^{(1)} \hat{r}_{ij} \cdot \underline{T}_i \cdot \underline{T}_j \cdot \hat{r}_{ij} \\ & + G_{ij}^{(2)} \hat{r}_{ij} \hat{r}_{ij} \hat{r}_{ij} \hat{r}_{ij} : \underline{T}_i \underline{T}_j) + \dots, \end{aligned} \quad (1)$$

where the parameters ϵ_{ij} , ξ_{ij} , J_{ij} , etc. depend only on the distance r_{ij} between molecules,

$$\underline{T}_i \equiv \vec{\Omega}_i \vec{\Omega}_j - \frac{1}{3} \mathbf{1}, \quad (2)$$

and

$$\hat{r}_{ij} = \vec{r}_{ij} / r_{ij}. \quad (3)$$

In the mean-field approximation, correlations between cells i and j ($i \neq j$) are neglected. We then wrote down the characteristic Helmholtz potential

$$\begin{aligned} A = A_0 + U_T - TS = A_0 + k_B T \langle \ln f_M \rangle + \sum_{i,j} \left(\langle n_i \rangle \langle n_j \rangle \epsilon_{ij} + \xi_{ij} [(\hat{r}_{ij} \cdot \hat{z})^2 - \frac{1}{3}] (\langle n_i \rangle s_j + s_i \langle n_j \rangle) \right. \\ \left. + J_{ij} s_i s_j \left[\frac{2}{3} + G_{ij}^{(1)} \left[\frac{1}{3} (\hat{r}_{ij} \cdot \hat{z})^2 + \frac{1}{9} \right] + G_{ij}^{(2)} \left[(\hat{r}_{ij} \cdot \hat{z})^2 - \frac{1}{3} \right]^2 \right] \right), \end{aligned} \quad (4)$$

and found the distribution function which minimized A subject to the constraints

$$\sum_{n_1, \dots, n_M} \int d\vec{\Omega}_1 \cdots d\vec{\Omega}_M f_M = 1, \quad (5)$$

and

$$\sum_i \langle n_i \rangle = N, \quad (6)$$

where $\langle n_i \rangle$ is the average occupation at cell i . We thus obtained a distribution function of the form

$$f_M = \prod_{i=1}^M \frac{\exp[\beta(\mu - \phi_i) n_i - \beta \mathcal{C}_i n_i P_2(\cos \theta_i)]}{(4\pi) \{ 1 + \exp[\beta(\mu - \phi_i) F(\beta \mathcal{C}_i)] \}}, \quad (7)$$

where μ is the chemical potential,

$$\phi_i = \sum_j \epsilon_{ij} \langle n_j \rangle + \xi_{ij} [(\hat{r}_{ij} \cdot \hat{z})^2 - \frac{1}{3}] s_j, \quad (8)$$

$$\begin{aligned} \mathcal{C}_i = & \sum_j \xi_{ij} [(\hat{r}_{ij} \cdot \hat{z})^2 - \frac{1}{3}] \langle n_j \rangle \\ & + J_{ij} s_j \left[\frac{2}{3} + G_{ij}^{(1)} \left[\frac{1}{3} (\hat{r}_{ij} \cdot \hat{z})^2 + \frac{1}{9} \right] \right. \\ & \left. + G_{ij}^{(2)} \left[(\hat{r}_{ij} \cdot \hat{z})^2 - \frac{1}{3} \right]^2 \right], \end{aligned} \quad (9)$$

and

$$F(x) \equiv \int_0^1 d\tau \exp[-x P_2(\tau)]. \quad (10)$$

\mathcal{C}_i and ϕ_i are the mean fields for s_i and n_i . After performing the "correct" spatial averages over nearest neighbors, and neglecting ϵ_{ij} , we rewrote (8) and (9) as

$$\phi_i = -VR' [s_i - \frac{1}{2} s_{i+1} - \frac{1}{2} s_{i-1}] \quad (11)$$

$$\begin{aligned} \mathcal{C}_i = & -V[4s_i + R(s_{i-1} + s_{i+1})] \\ & -VR' (\langle n_i \rangle - \frac{1}{2} \langle n_{i-1} \rangle - \frac{1}{2} \langle n_{i+1} \rangle). \end{aligned} \quad (12)$$

In effect, temperature is measured in units of V/k_B , k_B being Boltzmann's constant (see below), and R and R' are material parameters which can be reduced to linear combinations of J_{ij} , G_{ij} , and ξ_{ij} . Physically, R can be thought of as the ratio of the quadrupole-quadrupole-like (QQ) interaction between vertical and side-by-side pairs of cells; in effect, R is inversely related to molecular length. Likewise, R' can be thought of as the ratio of monopole-quadrupole-like interactions to the QQ interactions of side-by-side pairs of cells. Using Eqs. (7), (10), (11), and (12), we obtained four self-consistency equations

$$\langle n_i \rangle = \frac{e^{\beta(\mu - \phi_i)} F(\beta \mathcal{C}_i)}{(1 + e^{\beta(\mu - \phi_i)}) F(\beta \mathcal{C}_i)}, \quad (13)$$

and

$$s_i = - \langle n_i \rangle F'(\beta \mathcal{C}_i) / F(\beta \mathcal{C}_i), \quad (14)$$

where $i=1, 2$. (Note that the prime denotes the derivative.) Along with Eq. (6), we solved a self-consistent system of five equations in five unknowns: s_1 , s_2 , $\langle n_1 \rangle$, $\langle n_2 \rangle$, and μ_i . This was done numerically using a Newton-Raphson scheme and is outlined in detail in I.

At high temperatures T (small βV , where $\beta = 1/k_B T$) we found an isotropic phase such that $\langle n_1 \rangle = \langle n_2 \rangle = 0.5$ and $s_1 = s_2 = 0$. Upon lowering T (for large enough R and small R') we encountered another solution such that $s_1 = s_2 \neq 0$ and $\langle n_1 \rangle = \langle n_2 \rangle = 0.5$. This solution, which we associate with a nematic phase and which becomes stable at $\beta V = 4.54/(2+R)$ in a first-order NI transition, is analogous to the Maier-Saupe²² transition. At lower temperatures another solution, associated with a smectic phase with a periodicity of two cells, appears. Here, $s_1 \neq s_2 \neq 0$ and $\langle n_1 \rangle \neq \langle n_2 \rangle \neq 0.5$. The NS transition can be either first or second order; in general, for a small nematic temperature range and a large R' (R' couples the parameters s and n), the NS transition is more likely to be first order.

For sufficiently small R (very strong in-plane QQ coupling, i.e., relatively long molecular length) and/or large R' , a nematic phase never appears and a first-order SI transition occurs. All the qualitative behavior is consistent with experimental results on homologous series,²³ as well as being similar to results of other models^{24, 25} for bulk. These successes notwithstanding, our stated purpose was to develop a model which treats the behavior of bulk and interface in a unified way. In the next three sections we discuss these extensions of our model.

III. THIN FILMS

There have recently appeared¹⁴⁻¹⁸ numerous experimental papers on freely suspended thin smectic films. In all of these works it was found that the film thickness is quantized in discrete values, where the incremental thickness very closely corresponds to the smectic-A layer spacing.¹⁷ To model such a film we no longer deal with an infinite or semi-infinite lattice, but rather limit the extent of the lattice along the \hat{z} axis to M cells, where $M = 2N - 1$ and N is the number of smectic layers (i.e., molecules) in the film. A two-layer film ($N=2$), for example, would contain three cells ($M=3$) each of thickness $d/2$. At zero temperature the film would exhibit perfect smectic ordering, that is, occupation (1, 0, 1) [corresponding to $\langle n_1 \rangle, \langle n_2 \rangle, \langle n_1 \rangle$] along with orientational order $\langle P_2(\cos \theta_i) \rangle_c = 1$. (Note added: $\langle P_2(\cos \theta_i) \rangle_c$ is the conditional average, i.e., $s_i / \langle n_i \rangle$.) This behavior is shown pictorially in Fig. 1. Because of mirror

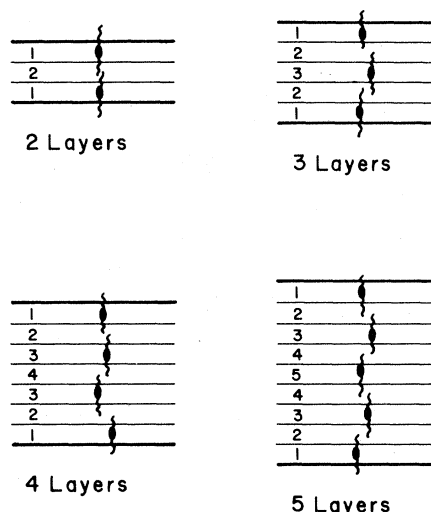


FIG. 1. Pictorial representation of films for $N=2, 3, 4$, and 5 with complete orientational and smectic-translational ordering. An N -layer film contains $2N-1$ cells, of which only N are independent due to mirror symmetry.

symmetry through the xy plane, an N -layer film contains only N independent cells; the labeling convention is also shown, where cell 1 represents the outermost cell and cell N the innermost. Films for $N=3, 4$, and 5 are also shown (at zero temperature), and the extension to thicker films is obvious.

Owing to the finite thickness of the system there need not be any requirement that solutions exhibit two-cell periodicity. Therefore, an N -layer film would necessitate solving $2N+1$ equations, that is, Eq. (13) and (14) for $i=1, \dots, N$, as well as Eq. (6). The $2N+1$ variables are, of course, s_i , $\langle n_i \rangle$, and μ ($i=1, \dots, N$). A given cell i , as in the bulk, interacts with four nearest-neighbor cells i , as well as with one cell each $i-1$ and $i+1$ [cf. Eqs. (11) and (12)]. However, at the surfaces, cell 1 can interact only with four other cells 1 and one cell 2; outside the film both s_0 and $\langle n_0 \rangle$ are zero, and hence we have the possibility for some rather interesting behavior. For example, since the R' term has the effect of coupling orientational order to nonuniformity in density, the presence of a surface (where $\langle n_1 \rangle$ is obviously larger than $\langle n_0 \rangle$) can, of course, result in enhanced orientational ordering. Another interesting effect concerns the available space in which the molecules can "spread out" for $T > 0$. In a two-layer film ($N=2$), for example, at $T=0$ two cells are occupied and one cell is empty. At higher temperatures, there are only three available cells in which to distribute the two molecules, unlike the bulk case in which there are $2N$ cells for N molecules. This entropic phenomenon has a tendency of inhibiting the film from "spread-

ing out" into a nematic, thus pushing smecticlike solutions to temperatures higher than those associated with bulk smectics. Moreover, because of interactions associated with R' , the surface plays the role of an external field which further stabilizes nonuniform solutions. Of course, these effects are counterbalanced by the reduced QQ interactions near the surfaces due to overall reduced mean fields \mathcal{H}_i and ϕ_i .

The system of simultaneous equations (6), (13), and (14) were solved as in I for films from two layers through thirteen to obtain the various sets of $\langle n_i \rangle$, s_i , and μ . Two cases were studied: $R = 0.79$, $R' = 0.43$, corresponding to the material cholesteryl myristate, and $R = 0.63$, $R' = 0.24$, corresponding to one possible (R, R') for 80CB (octyloxycyanobiphenyl). In bulk, the former exhibits a first-order nematic-smectic (NS) transition, whereas the latter is second order; both cases have been dealt with in bulk in I. (The parameters R and R' were fit to bulk thermodynamic data.) Since we have now removed the restriction on two-cell periodicity, a possibility exists for multiple smecticlike solutions in the films. Thus, we first investigate the numerical solutions which, at $T=0$, exhibit occupation $\langle n_i \rangle = (1, 0, 1, \dots, 0, 1)$; this solution we refer to as the bulklike smectic. We then look at the behavior of other numerical solutions, some of which are realistic and some of which are not.

For films of all thicknesses N , a perfect bulklike smectic solution always exists at low temperatures. For simplicity, we present results for a three-layer film for the material cholesteryl myristate. In Fig. 2(a) it is seen that, at low temperatures (T much smaller than any of the bulk transition temperatures) the occupation $\langle n_i \rangle$ configuration is very close to $(1, 0, 1, 0, 1)$. At higher temperatures, cells 1 and 3 begin to deplete and the pair of cells 2 begin to fill up, as in the case of a bulk smectic. Only in the vicinity of the bulk T_{NS} transition temperature do cells 1 and 3 begin to behave slightly different from each other; in this case the inner cell (3) tends to fill up at the cost of the outer cells (1). At some critical temperature T_c (which is a function of N) this class of solution disappears. At this point the solution, which represents a local minimum on a $2N+1$ dimensional free-energy hypersurface, is no longer a minimum. It could be pointed out that the feature $\langle n_i \rangle > \langle n_i \rangle$ near T_c is not universal; for sufficiently large R' , the reverse behavior was noted.

What is important, however, is that over a large temperature range this solution class is virtually identical to the bulk behavior. This can be seen in Fig. 3 in which we plot the average orientational

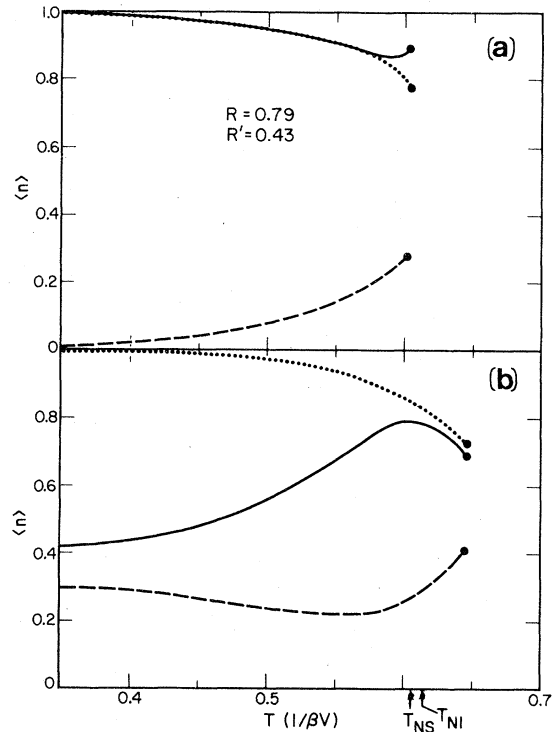


FIG. 2. Occupation ($\langle n_i \rangle$) versus temperature for two numerical solutions modeling a three-layer film of cholesteryl myristate. The top panel is the bulklike smectic solution, which exhibits perfect "smecticity" at zero temperature. The dotted line (\cdots) represents the outer cell 1, the broken line ($----$) cell 2, and the solid line ($—$) the inner cell 3. The lower panel represents another numerical solution. At low temperatures the behavior is unphysical, but at higher temperatures the behavior is similar to the bulklike smectic. Notice this solution exists at temperatures above the bulk NI-transition temperature.

order $1/N \sum_i s_i$, as might be measured by light, for the bulklike smectic class of solution. Although this parameter is consistently larger than in bulk, only near $T_c(N)$ does it deviate significantly from bulk behavior and, as N becomes large, the film order and bulk order are experimentally indistinguishable. One disturbing feature, however, is that for thicker films $T_c(N)$ is generally lower than the bulk NS transition temperature, and furthermore, does not appear to be asymptotically approaching bulk behavior.

In addition to the bulklike smectic solution, other numerical solutions are possible. For the same (R, R') as before, we show in Fig. 2(b) another numerical solution of the mean-field equations. At low temperatures the behavior is clearly absurd, since the density would peak near the surfaces but remain too low in the center of the film. Near T_c , however, the behavior of this solution

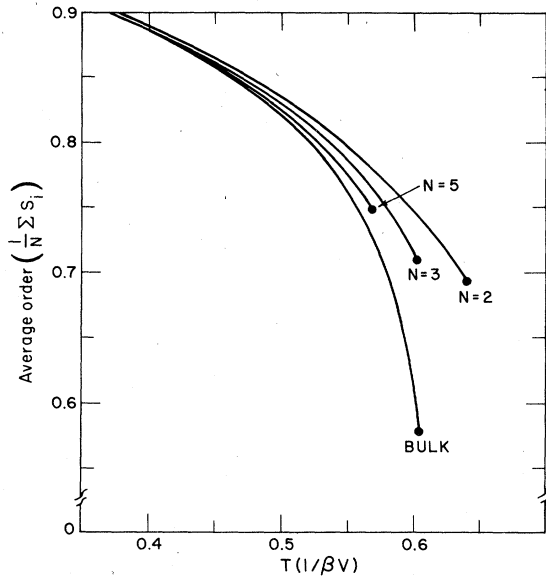


FIG. 3. Average orientational order (as measured by a long-wavelength probe such as light) of bulklike smectic versus temperature for films of cholesteryl myristate ($R = 0.79$, $R' = 0.43$). Notice enhanced ordering in thinner films ($N=2$), but approaching bulk in thicker films ($N=5$). For $N > 10$, there is virtually no difference in ordering from that of bulk.

is virtually identical to the bulklike smectic, not only with regard to $\langle n_i \rangle$, but also with s_i and $\langle P_2(\cos\theta_i) \rangle_c$ (see Figs. 4 and 5). Notice in addition that this solution can be taken to temperatures not only higher than T_C , but higher than T_{NS} and T_{NI} as well. In other words, a smecticlike state can exist in films at temperatures which would be smectic or even isotropic in the bulk, consistent with the experiment.¹⁷ At some temperature $T < T_C$, therefore, it's conceivable that a transition from one solution to another takes place. Since the average orientational order as measured by a long wavelength probe would be virtually indistinguishable for the two phases (see Fig. 6), the film would appear to possess essentially one smectic phase which can be taken to very high temperatures.

It should be pointed out that the free energy A for the bulklike smectic remains consistently lower (i.e., more stable) than the second solution from $T=0$ right up through T_C . In the vicinity of T_C the difference in free energies ΔA for the two solutions is extremely small, roughly the equivalent of the change in free energy of one of the solutions if the temperature were changed by 20 mK. The thermodynamics of such a phase transition from the bulklike smectic to another solution will be examined in detail in Sec. V.

Materials which are characterized by a second-

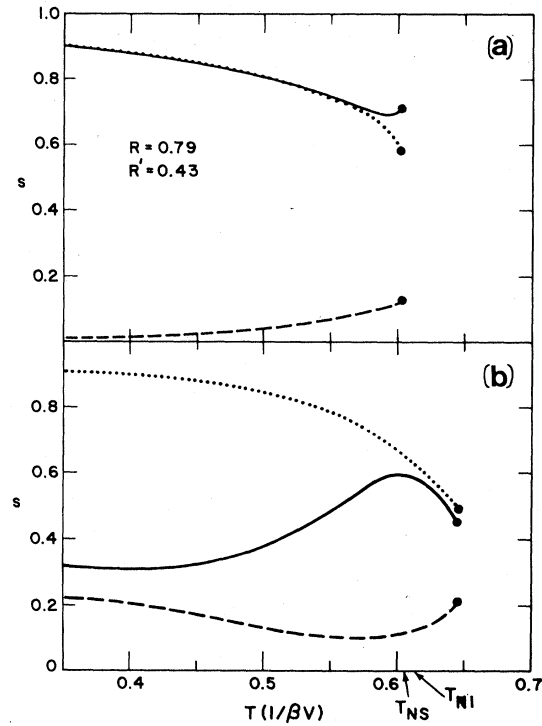


FIG. 4. s_i versus temperature; otherwise the same as Fig. 2.

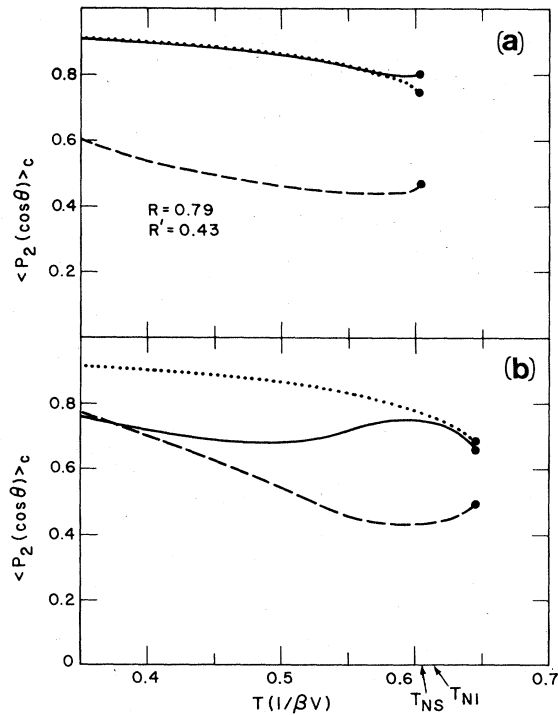


FIG. 5. Conditional order $\langle P_2(\cos\theta) \rangle_c$ versus temperature; otherwise the same as Fig. 2.

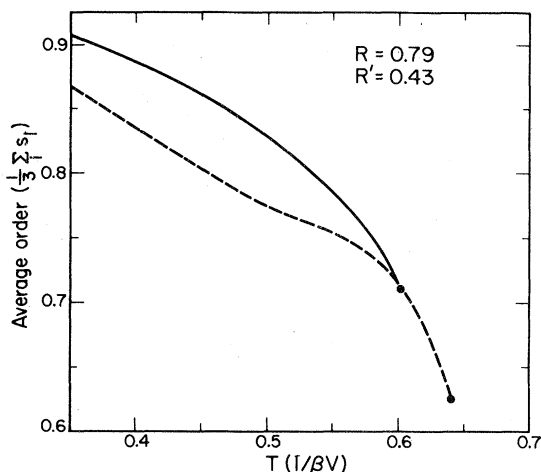


FIG. 6. Average orientational order versus temperature for two numerical solutions of cholesteryl myristate in a three-layer film. The solid line represents the bulklike smectic, and the broken line represents a second solution as shown in Fig. 2(b). Near T_C , the temperature above which the bulklike solution no longer exists, the two solutions would be indistinguishable experimentally.

order NS bulk transition exhibit qualitatively similar behavior. In Fig. 7 we show $\langle n_i \rangle$ for 80CB, which is second order in bulk. Note, in fact, that when the smecticlike solution vanishes it again does so discontinuously (i.e., first-order behavior). Since the kinetics and stabilizing forces of these LC films are not well understood and, to our knowledge, freely-suspended *thin* films have not been observed in other than smectic phases, we assume that when smecticlike solutions no longer exist the film ruptures. This phenomenon is treated elsewhere.²⁶

For thicker films we observe essentially the same qualitative behavior as in thinner ($N=3$) films, namely, one bulklike smectic and several other solutions. (The number of numerical solutions dramatically increases with increasing N). When N becomes large ($N \geq 8$), some of the other smecticlike solutions (which can be taken up to temperatures greater than T_C) appear virtually identical, cell-by-cell, to the bulklike smectic. This behavior may be the solution to the dilemma that $T_C(N)$ does not appear to converge on T_{NS} . In addition, there are still other smecticlike solutions which can exist at $T > T_{NS}$. Still other classes of solutions exist which, although appearing quite stable by the free-energy A criterion, are physically inaccessible. For example, we obtain a solution in which all the molecules condense into a small region of the film, thereby increasing U without great cost to the entropy term in the free energy [cf. Eq. (4)]. Such a solution would possess

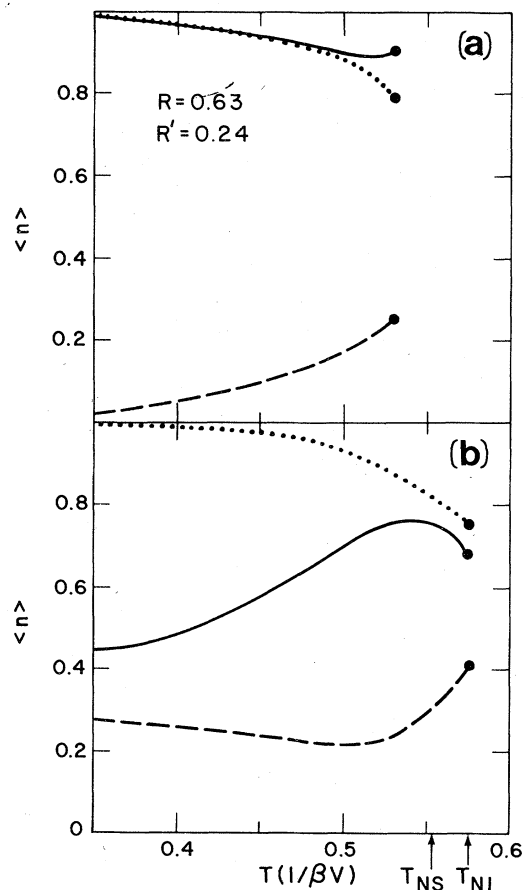


FIG. 7. $\langle n_i \rangle$ versus temperature for three-layer film of one possible (R, R') modeling 80CB. Top and bottom panels same as in Fig. 2. Notice that numerical solutions of film end discontinuously, whereas the bulk exhibits a second-order NS transition.

an enormous mass density and is clearly unphysical. It seems clear that such solutions arise from the omission of excluded volume effects inherent in mean-field theory; this question will be addressed in Sec. V. In addition, it should be pointed out that, at least in the case of thinner films ($N < 5$), no nematiclike solution appears, except possibly for those nonphysical "condensed" solutions just discussed. However, at very high temperatures, solutions similar to the bulk isotropic exist. Nevertheless, for $\beta V > 0$ and $R' > 0$, some degree of orientational ordering takes place due to surface interactions.

To summarize, when the model is adapted to thin systems with two free surfaces, we find smecticlike solutions which can be taken to unusually high temperatures [i.e., $T > T_{NI}$ (bulk)] consistent with experiments. In addition, the possibility for a smectic-smectic transition exists, where the two phases would be virtually indistinguishable

in any experiment using a long-wavelength probe. We also predict that materials which possess a second-order NS transition in bulk can have their smecticlike phase in films vanish discontinuously, with associated rupture of the film. Finally, we also predict the possibility of orientational order enhanced by the presence of surfaces (cf. Fig. 3), which is again consistent with one explanation of experimentally-observed behavior¹⁷ in films. (This topic will be amplified in the next section.) Although in Sec. V we discuss some of the drawbacks and inconsistencies of the model, we nevertheless feel that the qualitative aspects are essentially correct, and that our model is useful in predicting and understanding behavior in thin films.

IV. INDUCED ORDER AT THE ISOTROPIC INTERFACE

At the surface (either free or solid) of an isotropic liquid-crystal, isotropy is broken. As was discussed in the introduction, this can induce orientational ordering, which should decay as one moves into the bulk of the fluid. The amount of ordering induced, and the length over which it persists, can be analyzed within the context of our model, and is the subject of this section.

Consider a semi-infinite lattice, whose outermost layer is labeled by $i=1$, and where i increases into the bulk of the system. We assume that the mean-field equations, Eqs. (11)–(14), are valid, even near the surface. Of course, at the outermost layer ($i=1$) the mean fields ϕ_i and \mathcal{C}_i are not defined unless we specify s_0 and $\langle n_0 \rangle$ (i.e., impose boundary conditions). For a free surface, clearly $\langle n_0 \rangle = 0$ and $s_0 = 0$. For prepared glass surfaces $\langle n_0 \rangle$ and s_0 can take nonzero values, depending upon surface treatment, subject to $-\frac{1}{2} \leq s_0 / \langle n_0 \rangle \leq 1$. Before considering some numerical examples, a theoretical analysis of the surface ordering is presented.

When R' is zero, it is easy to verify that any free surface has no effect on the isotropic phase. That is, $s_i = 0$ and $\langle n_i \rangle = \text{constant}$ solves the mean-field equations [cf. Eqs. (11)–(14)]. For sufficiently weak coupling between orientation and density (i.e., small R'), a perturbation analysis of the degree of rotational ordering should be possible. This should also be the case at a solid surface, provided that the surface order is small.

Denoting the deviation from the isotropic phase values by $\delta \langle n_i \rangle$, δs_i , $\delta \beta \mathcal{C}_i$, and, $\delta \beta \phi_i$, and linearizing Eqs. (13) and (14) about the isotropic solution, we obtain

$$\delta \langle n_i \rangle = -\frac{1}{4} \delta \beta \phi_i, \quad (15)$$

and

$$\delta s_i = -\frac{1}{10} \delta \beta \mathcal{C}_i. \quad (16)$$

Moreover, from Eqs. (11) and (12) it follows that

$$\delta \beta \phi_i = -\beta V R' [\delta s_i - \frac{1}{2} (\delta s_{i+1} + \delta s_{i-1})], \quad (17)$$

and

$$\begin{aligned} \delta \beta \mathcal{C}_i = & -\beta V R' [\delta \langle n_i \rangle - \frac{1}{2} (\delta \langle n_{i+1} \rangle + \delta \langle n_{i-1} \rangle)] \\ & - \beta V [4 \delta s_i + R (\delta s_{i+1} + \delta s_{i-1})]. \end{aligned} \quad (18)$$

Of course,

$$\delta s_0 \equiv s_0, \quad (19)$$

and

$$\delta \langle n_0 \rangle \equiv (\langle n_0 \rangle - \frac{1}{2}), \quad (20)$$

where s_0 and $\langle n_0 \rangle$ are the imposed order and density of the surface layer (they both vanish at a free surface).

Eliminating the density from Eqs. (15)–(18) yields

$$\delta s_{i+2} + \delta s_{i-2} + \gamma_1 (\delta s_{i+1} + \delta s_{i-1}) + \gamma_0 \delta s_i = 0, \quad (21)$$

where

$$\gamma_0 \equiv \frac{-160}{(\beta V R')^2} \left\{ 1 - \frac{1}{10} \beta V [4 + \frac{3}{8} \beta V (R')^2] \right\}, \quad (22a)$$

and

$$\gamma_1 \equiv \frac{16}{\beta V (R')^2} \left\{ R - \frac{1}{4} \beta V (R')^2 \right\}. \quad (22b)$$

It is straightforward to show that the solution to Eq. (21), satisfying Eqs. (19) and (20), and decaying into the bulk is

$$\delta s_i = A_+ \lambda_+^i + A_- \lambda_-^i, \quad (23)$$

and [cf. Eqs. (15) and (16)]

$$\begin{aligned} \delta \langle n_i \rangle = & \frac{1}{16} \beta V R' \left\{ A_+ \lambda_+^i \left[4 + \gamma_1 - [\gamma_1^2 - 4(\gamma_0 - 2)]^{1/2} \right] \right. \\ & \left. + A_- \lambda_-^i \left[4 + \gamma_1 + [\gamma_1^2 - 4(\gamma_0 - 2)]^{1/2} \right] \right\}. \end{aligned} \quad (24)$$

In Eqs. (23) and (24),

$$A_{\pm} \equiv \frac{1}{2} s_0 \pm \frac{[s_0(\gamma_1 + 4) - 16\delta \langle n_0 \rangle / (\beta V R')]}{2[\gamma_1^2 - 4(\gamma_0 - 2)]^{1/2}}, \quad (25a)$$

and

$$\begin{aligned} \lambda_{\pm} \equiv & -\frac{1}{4} \left\{ -\lambda_1 \pm [\gamma_1^2 - 4(\gamma_0 - 2)]^{1/2} \right\} \\ & \times \left\{ 1 - \left[1 - \left(\frac{4}{-\gamma_1 \pm [\gamma_1^2 - 4(\gamma_0 - 2)]^{1/2}} \right)^2 \right]^{1/2} \right\}. \end{aligned} \quad (25b)$$

It can be shown that as long as the isotropic phase is stable (or metastable), then $|\lambda_{\pm}| < 1$. When the limit of stability is reached (see Sec. IV of Ref. 21), one of the λ 's becomes equal to unity. For a free surface

$$A_{\pm} = \pm \frac{4}{\beta VR' [\gamma_1^2 - 4(\gamma_0 - 2)]^{1/2}}. \quad (26)$$

A few comments are in order. First, note that the λ_{\pm} are even functions of R' . That is, the characteristic decay lengths do not depend on the sign of the density/orientation coupling. Second, the induced order proportional to s_0 is independent of the sign of R' , while that involving $\delta\langle n_0 \rangle$ is odd in R' . Thus, at a free surface, whether or not the molecules tend to "stand up" ($\delta s > 0$) or "lie down" ($\delta s < 0$) is governed by the sign of R' . This behavior is quite reasonable, given the form of the mean fields given in Eqs. (11) and (12). Finally, in the limit of $R' \rightarrow 0$,

$$A_{\pm} \sim \frac{1}{2} s_0 \pm \frac{1}{2} \frac{R}{|R|} \left(s_0 - \frac{R'}{R} \delta\langle n_0 \rangle \right), \quad (27a)$$

$$\lambda_{\pm} \sim \frac{5(1 - 2/5\beta V)}{\beta VR} \times \left\{ 1 - \left[1 - \left(\frac{\beta VR}{5(1 - 2/5\beta V)} \right)^2 \right]^{1/2} \right\}, \quad R > 0, \quad (27b)$$

and

$$\lambda_{\pm} \sim \beta V(R')^2/16R, \quad R > 0. \quad (27c)$$

Therefore, except at the surface, the terms proportional to λ_{\pm}^i in Eq. (23) can be neglected and hence

$$\delta s_i \sim [s_0 - \frac{1}{2}(R'/R)\delta\langle n_0 \rangle] \lambda_{\pm}^i, \quad R > 0, \quad R' \rightarrow 0. \quad (28)$$

Equation (28) shows that the order decays monotonically away from the surface ($\lambda_{\pm} > 0$), and the decay length is independent of R' for small R' , going to infinity at the isotropic supercooling limit (see Sec. IV of I for a discussion of the stability of the bulk phase). Before presenting an example, we describe the procedure used when the surface

ordering is not weak.

The perturbative analysis presented above must fail when either R' or s_0 is too large. Since the induced order decays rather quickly into the bulk, a numerical solution of the mean-field equations can be carried out. We numerically solved the mean-field equations, for a system of N cells, fixing the order parameters of the $(N+1)^{\text{st}}$ cell to be isotropic and those of the zeroth cell to have values appropriate for either a free or solid surface. Also the chemical potential was set equal to its isotropic value (i.e., $\mu = 0$). N was increased until convergence was obtained.

Table I shows results for the case $R = 0.49$, $R' = 0.12$ and free-surface boundary conditions. As the temperature approached the bulk isotropic supercooling limit, it became increasingly difficult to get the numerical procedure to converge. The example in Table I (the parameters could correspond to the material 80CB (Ref. 21) shows that even below the NI transition, the degree of surface ordering is small. It is described by the perturbative theory to within about 20% at higher temperatures and gets progressively worse as the supercooling limit is approached. Furthermore, it decays to zero over one or two molecular lengths.

As was discussed above, any ordering at a free surface, for the type of interaction assumed here, results from R' being nonzero. The nature of R' lies in quadrupolar or polarization anisotropy forces. In this work, we have assumed that the molecules have inversion symmetry, and thus no dipolar interactions are present. If this were not the case, then the forces with the symmetry of a charge/dipole interaction would also lead to surface ordering. Although such effects can easily be incorporated into our model, we do not do so here.

TABLE I. s_i vs. T/T_{NI} at a liquid-crystal-air interface for a semi-infinite sample in the isotropic phase. These results are for one possible set of parameters for 80CB ($R = 0.49$, $R' = 0.12$). Columns a represent the numerical calculation and columns b the perturbative [cf. Eq. (23)] results. Note increasing decay length at lower temperatures. (The supercooling temperature T^* is given by $T^*/T_{\text{NI}} = 0.908$.)

T/T_{NI}	$s_1 (10^{-2})$		$s_2 (10^{-2})$		$s_3 (10^{-2})$		$s_4 (10^{-2})$		$s_5 (10^{-2})$	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
1.005	2.76	2.26	1.07	0.82	0.40	0.30	0.15	0.11	0.05	0.04
1.000	2.86	2.32	1.15	0.87	0.44	0.33	0.17	0.12	0.06	0.05
0.995	2.99	2.38	1.23	0.91	0.49	0.35	0.19	0.14	0.07	0.05
0.990	3.12	2.44	1.34	0.96	0.55	0.38	0.22	0.15	0.09	0.06
0.985	3.28	2.50	1.46	1.01	0.62	0.41	0.26	0.17	0.10	0.07
0.980	3.46	2.57	1.61	1.07	0.70	0.45	0.30	0.19	0.13	0.08
0.975	3.68	2.65	1.79	1.13	0.82	0.49	0.36	0.21	0.16	0.09
0.966	4.41	2.81	2.44	1.27	1.22	0.58	0.58	0.27	0.27	0.12

V. DISCUSSION

The model presented in I, and its application to interfacial and thin-film phenomena without introducing new parameters, has been qualitatively successful. Because of orientational and translational coupling (R'), we have shown that surface ordering can be enhanced from that of the bulk. In the bulk isotropic phase, values of s_i near the air interface are nonzero, decaying to zero in the bulk with some characteristic length ξ . Similarly, if other boundaries are imposed, the order decays to zero from some value s_0 at the surface. As expected, this characteristic length for both boundary conditions is generally quite small, in agreement with available experimental results.⁷ (However, ξ does diverge near the isotropic supercooling temperature.)

In addition, we have presented a perturbative calculation for the case of small order parameter deviations from the isotropic phase. As with the numerical results, we found that ξ diverges near the isotropic supercooling limit. Furthermore, for the case of small R' , we found that ξ is independent of R' . The numerical results, in general, were in qualitative agreement with the perturbative analysis. Although as the supercooling limit was approached, the numerical method became increasingly more difficult to apply.

For the case of thin films (two free surfaces), many numerical solutions were found, corresponding to extrema on a $2N+1$ dimensional free-energy hypersurface. Although many of the solutions are unphysical, we found (for each N) one solution which is a bulklike smectic in the limit of low temperature. Other solutions were also found, which are quantitatively very similar to the bulklike smectic at higher temperatures and which can be taken, in some cases, above even T_{NI} . If transitions are possible from one solution to another, then we have shown that smectic films may indeed be taken to temperatures above the bulk NS and/or NI transition, in agreement with the experiment.¹⁷ Furthermore, we also find that in systems which in bulk exhibit second-order NS behavior, the smecticlike film solutions disappear in a discontinuous manner. In addition, in thicker films we found surface ordering effects qualitatively similar to systems with one free surface. For small N , the surfaces enhance the orientational order of the film from that of bulk. For thicker films, and away from the surfaces, the bulklike smectic order parameters approach their bulk values for large N . The order parameters for other smecticlike film solutions are also similar to what is encountered in bulk and, indeed, it would be extremely difficult to experimentally sort out

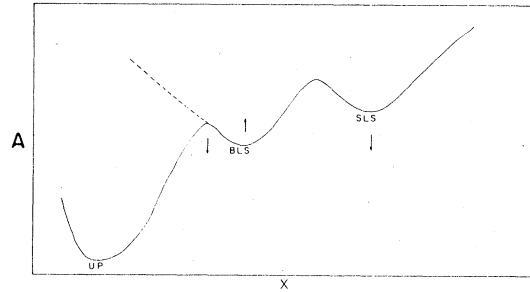


FIG. 8. Free-energy A versus order-parameter X , where X represents some direction in order-parameter space. UP, the unphysical solution, has the deepest minimum without the incorporation of excluded volume effects. If such effects are included, this minimum disappears (dashed line). BLS is the bulklike smectic solution and SLS the smecticlike solution.

the multitude of smecticlike phases using a long-wavelength probe.

Despite the many qualitative successes, there are a number of practical and theoretical problems which must be addressed. The existence of energetically favorable but unphysical solutions in which the molecules "condense" into a small region of the lattice is rather unsettling. In addition, we have also suggested in Sec. IV the possibility of a transition between two film solutions which are very close, although not quite equal, in free energies; this behavior is, thermodynamically unacceptable. The source of these problems lies in the mean-field approximation, which neglects short-range correlations and, thus, excluded volume. How the inclusion of excluded volume might eliminate those problems can be seen by the following heuristic argument.

For an N -layer film, we schematically represent in Fig. 8 the projection of the free-energy hypersurface along some direction x (e.g., s_i , $\langle n_i \rangle$, etc.). Shown are three minima, corresponding to the bulklike smectic solution (BLS), another smecticlike solution (SLS), and an unphysical solution (UP) in which the local density is too high. For the temperature in Fig. 8, the BLS is more stable than the SLS, but both are considerably less stable than the unphysical solution. As the temperature is raised, the BLS free energy approaches that of the SLS, and the "barrier" between the BLS and unphysical solution decreases. Unfortunately, this barrier disappears just before the free energies of SLS and BLS become equal, thereby causing BLS no longer to be a minimum. In principle a transition to the smecticlike solution cannot take place, and one would expect the film to rupture since there are no physically accessible smecticlike states. (In practice, the difference in free-energy ΔA is so small as to be insignificant in

light of the approximations made in this work.)

It is clear that the excluded volume energy of the unphysical solutions should be huge, while being relatively small for the smecticlike solutions. Thus with the inclusion of some aspects of excluded volume, the unphysical minimum should vanish, and the BLS solution should exist to the slightly higher temperature where its free energy equals that of the SLS. One way in which this short-range order can be included is by using the self-consistent mean-field theories originally developed for spin systems.²⁷

Such an extension is currently under investigation. It should be noted, that in all of the mean-field calculations for the bulk behavior, the spatial periodicity of the density is assumed. This precludes the possibility of encountering the solutions in which the density is too high.

Various other objections to our present work can also be made. Nowhere have we considered the static forces and kinetics stabilizing of the film. Although the literature is vast²⁸ in the area of isotropic films (such as soap bubbles), the question of film stability and "correct" thermodynamic functions (such as surface tension) in (layered) liquid-crystal films is beyond the scope of this work. We have assumed that the film is a constant volume system at fixed chemical potential and temperature, and thus its stability is characterized by the Helmholtz potential. Moreover, when no smecticlike solution exists, we assume that the film is no longer stable against rupture. We know of no experiments in which *thin* nonsmectic films were stabilized, although thick nematic films have, in fact, been studied.⁴⁻⁶

VI. CONCLUSIONS

We have applied our lattice model²¹ to interfaces and thin films, obtaining qualitative agreement with other theories and experiment. However, unlike past works, we have presented bulk, interfaces, and films in a single unified model, without the necessity of introducing new parameters or equations. In principle, either a knowledge of the molecular pair potential or the experimental determination of various quantities in bulk (such as T_{NI} , T_{NS} , etc.) is sufficient to determine the two material parameters R and R' . In I, the latter approach was taken. Once these have been set, as has been shown here, the extension to interfaces and films is unambiguous.

Some difficulties, of course, do exist. By and large they can be remedied with the incorporation of excluded volume effects, necessitating going beyond the mean-field approximation. Nevertheless these improvements should have little qualitative effect on the physically reasonable behavior predicted in mean field. Work is currently underway to go beyond the mean-field approximation, as well as to study other liquid-crystalline phases.

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