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Mean-field theory of the nematic–smectic-A phase change in liquid crystals

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The problem of the first- or second-order nature of the nematic–smectic-A phase change is explored. It is found that couplings between various order parameters, especially the first and second translational ones, are important. General Landau theory for coupled orientational and translational order parameters is developed. Numerical methods and results for translational ordering are presented. The effects of molecular polarity are considered. The relative importance of different couplings is discussed, and some experiments are proposed.

I. INTRODUCTION

In the nematic liquid crystalline phase, barlike molecules have a uniform center of mass distribution but have their long axes aligned along a specific direction in space, often indicated by a unit vector, the "director." In the smectic-A phase, the molecules coalesce into equidistant planes perpendicular to the nematic director; the center-of-mass density is thus periodic in the dimension perpendicular to the planes and uniform in the other two. McMillan[1,2] was the first to point out that the transition between these two phases could be second order. He carried out a variational calculation for a system with a Gaussian interparticle potential and found that for a certain range of potential parameters, the parameter characterizing smectic order grows continuously from zero below the nematic to smectic-A transition temperature T_{NA}. For other potential parameters, the smectic order jumped discontinuously at T_{NA}. McMillan concluded that the transition could be second order only when nematic order was nearly saturated at T_{NA}. Systems with a large difference between the isotropic to nematic transition temperature T_{NI} and T_{NA} are therefore expected to be the best candidates for a second-order smectic to nematic transition.

The center-of-mass density is periodic in the direction perpendicular to the smectic planes in the smectic-A phase. It can, therefore, be expanded in a Fourier series of wave number $q_0 = 2\pi/d$, where d is the interplanar spacing. de Gennes[3,4] has pointed out that the smectic order parameter is the first Fourier coefficient, $\tilde{\rho}_1$, in this series. Since $\tilde{\rho}_1$ has both an amplitude and a phase, the smectic-A order parameter is a complex number. It, therefore, has the same symmetry as the superfluid or superconducting order parameter. In fact, there is a strong analogy between a smectic-A liquid crystal and a superconductor with the molecular director in the former playing the role of the vector potential in the latter. Traditional reasoning would then say that the nematic to smectic-A transition should be second order and by universality the critical exponents for this transition should be the same as those for the superfluid or superconducting transition.[5] Coupling of $\tilde{\rho}_1$ to other fields can, however, make the coefficient of $|\tilde{\rho}_1|^4$ in a Landau-Ginzburg expansion of the free energy negative and lead to a first-order transition just as in the Rodbell-Bean effect[6] in magnetic transitions. de Gennes has analyzed the smectic to nematic transition, including couplings of $\tilde{\rho}_1$ to the nematic order within the context of the Landau mean-field theory and concluded that the transition is more likely to be second order the smaller T_{NA}/T_{NI}.[4]

The purpose of this paper is to investigate more thoroughly the nematic to smectic-A transition within mean-field theory. Our primary interest will be to investigate as generally as possible those factors which determine whether the transition is first or second order. Our approach will be on two fronts. First, we will consider the transition within the context of the most general Landau mean-field theory. Second, we will solve numerically the Euler equations for various interparticle potentials for systems with saturated nematic ordering. Our principal conclusion is that two factors control the nature of the transition. The first factor is the one discussed by McMillan and de Gennes: a second-order transition is more likely when T_{NA}/T_{NI} is small, and order is saturated. The second factor is the tendency of the system to order with interplanar spacing $\frac{1}{2}d$ and order parameter $\tilde{\rho}_2$. If T_2^* is the transition temperature for $\frac{1}{2}d$ ordering, the nematic to smectic-A transition is more likely to be second order when T_2^*/T_{NA} is small or negative. Possible prescriptions for realizing this criterion are suggested.

This paper is divided into eight sections of which this is the first. Section II treats the Landau theory of the nematic to smectic-A transition when nematic order is saturated. Criteria for a first- or second-order transition or a tricritical point are obtained. Section III treats the complete Landau theory including all possible couplings of $\tilde\rho_1$ to other positional, orientational, and mixed order parameters. This treatment emphasizes the necessity of having a complete picture of the nematic phase just above T_{NA} before quantitative information about the nematic to smectic-A transition can be obtained. Section IV treats a molecular-field model with saturated nematic order using the general results of Sec. II. This model is essentially the one studied by Kirkwood and Monroe,[7] McMillan,[1,2] and Lee *et al.*[9] Section V discusses numerical methods of solving molecular-field models with saturated nematic order. These methods are not restricted to small order parameters as is the Landau theory. Two methods are discussed: the Fourier-series truncation scheme used by Kobayashi,[8] McMillan,[1,2] and Lee *et al.*[9] and an iteration scheme introduced here. Numerical results from the iteration scheme are presented. Section VI considers numerical methods involving both orientational and translational order. Shortcomings of the Fourier truncation scheme are discussed. Section VII treats polar systems. Section VIII summarizes important conclusions and makes some predictions based on these conclusions.

II. LANDAU THEORY WITH SATURATED NEMATIC ORDER

In this section we will consider a model of the nematic to smectic-A transition which ignores orientational ordering (i.e., assumes orientational order has been saturated) but includes higher Fourier components of the density. Let $\vec{r}^{\,\alpha}$ be the position of the center of mass of molecule α. We assume here that the molecule is symmetric, so its center of mass is also its geometric center. The center-of-mass density is then

$$\rho(\vec{r}) = \left\langle \sum_\alpha \delta(\vec{r} - \vec{r}^{\,\alpha}) \right\rangle , \tag{2.1}$$

where the angular brackets signify an average with respect to the equilibrium density matrix of the system. In the smectic-A phase, $\rho(\vec{r})$ can be expanded in a Fourier series of period d, the interplanar spacing:

$$\begin{aligned}(\rho) &= \rho_0 + \sum_{n>0} \rho_n \cos n(\vec{q}_0 \cdot \vec{r} + \phi) , \\ &= \rho_0 + \frac{1}{2} \sum_{n>0} (\rho_n e^{in\phi} e^{in\vec{q}_0 \cdot \vec{r}} + \text{c.c.}) ,\end{aligned} \tag{2.2}$$

where $\vec{q}_0$ is a vector of magnitude $q_0 = 2\pi/d$ normal to the smectic planes and ϕ is a phase shift which specifies the coordinate-system origin. $\tilde\rho_n$ is just the average of the nth Fourier component of the density:

$$\rho_n = 2\rho_0 \frac{1}{N} \left\langle \sum_\alpha \cos n\vec{q}_0 \cdot \vec{r}^{\,\alpha} \right\rangle . \tag{2.3}$$

The smectic-A phase is thus described by an infinite series of order parameters:

$$\tilde\rho_n = \rho_n e^{in\phi} . \tag{2.4}$$

$\tilde\rho_1$ is the smectic-order parameter discussed by de Gennes. The higher Fourier components in general have a nonzero amplitude in the smectic state, but their phase is controlled by the phase of ρ_1, as indicated in Eq. (2.4).

A phenomenological free-energy density F can be constructed from the $\tilde\rho_n$ subject only to the constraints that F have a high-temperature minimum with all $\tilde\rho_n = 0$ for $n > 0$, that F be positive for large $\tilde\rho_n$, and that it be invariant with respect to uniform translations of the variable ϕ. The last constraint is merely the statement that the free energy should not depend on where we choose the origin of our coordinate system. Hence the only contributions of $\tilde\rho_n$ which are admissible in F are those which have no phase dependence, i.e., combinations of the form

$$\prod_{i=1}^{k} (\rho_{n_i})^{a_i} \prod_{i=1}^{k'} (\rho_{n_j}^*)^{a_j} ,$$

where

$$\sum_{i=1}^{k} n_i a_i = \sum_{j=1}^{k'} n_j a_j ,$$

where a_i and a_j are integers.

We will consider now a model free energy in which only the order parameters ρ_1 and ρ_2 appear, reserving a discussion of the effects of higher-order ρ_n's for Sec. III. The most general free-energy density to fourth order in ρ_1 and ρ_2 is

$$\begin{aligned}F = {} & \tfrac{1}{2} A_1 \rho_1^2 + \tfrac{1}{2} A_2 \rho_2^2 + \tfrac{1}{4} B_1 \rho_1^4 + \tfrac{1}{4} B_2 \rho_2^4 \\ & + u\rho_1^2 \rho_2^2 - t\rho_1^2 \rho_2 .\end{aligned} \tag{2.5}$$

A_1 and A_2 change sign at the ordering temperatures T_1^* and T_2^* of the free ρ_1 and ρ_2 fields:

$$A_1 = a_1(T - T_1^*) , \quad A_2 = a_2(T - T_2^*) . \tag{2.6}$$

The nematic to smectic-A transition is driven by fluctuations in $\tilde{\rho}_1$ so that T_1^* is presumably greater than T_2^* or the ordering temperature of any of the other ρ_n's.

F must be a minimum with respect to variations in ρ_1 and ρ_2:

$$\frac{\partial F}{\partial \rho_1} = A_1\rho_1 + B_1\rho_1^3 - 2t\rho_1\rho_2 + 2u\rho_1\rho_2^2 = 0\,, \qquad (2.7\text{a})$$

$$\frac{\partial F}{\partial \rho_2} = A_2\rho_2 + B_2\rho_2^3 - t\rho_1^2 + 2u\rho_1^2\rho_2 = 0\,. \qquad (2.7\text{b})$$

Equation (2.7b) can be solved for ρ_2 in terms of ρ_1. In the neighborhood of the transition ρ_1 is small, and we need only consider ρ_2 to lowest order in ρ_1:

$$\rho_2 = (t/A_2)\rho_1^2 + O(\rho_1^4)\,. \qquad (2.8)$$

Note that A_2 is positive in the vicinity of T_1^* so that the sign of ρ_2 is controlled by the sign of t. Inserting expression (2.8) for ρ_2 into Eq. (2.5) for the free energy, we obtain a new free energy which is a function of ρ_1 only:

$$F = \tfrac{1}{2}A_1\rho_1^2 + \tfrac{1}{4}(B_1 - 2t^2/A_2)\rho_1^4 + \tfrac{1}{6}C_1'\rho_1^6\,, \qquad (2.9)$$

where we have added a sixth-order term to insure stability. The nature of the nematic to smectic-A transitions is controlled by the sign of the coefficient of ρ_1^4. The transition is second order, first order, or tricritical according to whether $B_1' = B_1 - 2t^2/A_2$ is positive, negative, or zero. If B_1' is positive (second order)

$$\rho_1 = \left[\frac{a_1}{B_1'}(T_1^* - T)\right]^{1/2}, \quad \rho_2 = \frac{ta_1}{A_2B_1'}(T_1^* - T)\,. \qquad (2.10)$$

If $B_1' = 0$, there is a tricritical point with

$$\rho_1 = \left[\frac{a_1}{C_1'}(T_1^* - T)\right]^{1/4}, \quad \rho_2 = \frac{t}{A_2}\left[\frac{a_1}{C_1'}(T_1^* - T)\right]^{1/2}. \qquad (2.11)$$

If $B_1' < 0$, the transition is first order and occurs at a temperature T_{c1} greater than T_1^*. ρ_2 is still proportional to ρ_1^2 in this approximation.

As long as A_2 is positive (i.e., as long as ρ_1 orders at higher temperature than the free ρ_2), B_1' is always less than B_1. The effect of the coupling of ρ_1 to ρ_2 is to increase the tendency for the transition to be first order. We shall see that this feature is general. Any field σ which has a coupling to ρ_1 of the form $\sigma\rho_1^2$ will reduce the effective value of B_1 and increase the probability of a first-order transition.

III. GENERALIZED LANDAU THEORY

Orientational as well as positional ordering of long bar molecules can be described in terms of the distribution function

$$f(\vec{r}, \Omega) = \left\langle \sum_\alpha \delta(\vec{r} - \vec{r}^{\,\alpha})\delta(\Omega - \Omega^\alpha) \right\rangle, \qquad (3.1)$$

where $\Omega^\alpha = (\theta^\alpha, \phi^\alpha)$ specifies the orientation of molecule α. $f(\vec{r}, \Omega)$ satisfies the normalization condition

$$\int d\Omega\, f(\vec{r}, \Omega) = \rho(\vec{r})\,. \qquad (3.2)$$

In the smectic-A state, $f(\vec{r}, \Omega)$ can be expanded in terms of $\cos n(\vec{q}_0 \cdot \vec{r} + \phi)$ and even-order Legendre polynomials

$$f(\vec{r}, \Omega) = \frac{\rho_0}{4\pi} + \sum_{nm} \sigma^{nm} \cos n(\vec{q}_0 \cdot \vec{r} + \phi)\, \frac{4m+1}{4\pi} P_{2m}(\cos\theta)\,, \qquad (3.3)$$

where

$$\sigma^{nm} = 2\rho_0 \frac{1}{N} \sum_\alpha \langle \cos n\vec{q}_0 \cdot \vec{r}^{\,\alpha} P_{2m}(\cos\vartheta^\alpha)\rangle\,. \qquad (3.4)$$

The expansion (3.4) assumes that the molecular ordering is inversion and azimuthally symmetric. An expansion including other Y_{lm}'s would be needed if there were vector or biaxial ordering. Note that

$$\sigma^{n0} = \rho_n\,; \qquad (3.5\text{a})$$

$$\sigma^{0m} = 2\rho_0\langle P_{2m}\rangle\,. \qquad (3.5\text{b})$$

An alternate form of Eqs. (3.5) in terms of irreducible tensors will make more convenient the isolation of scalar invariants to appear in a free-energy density. Let ν_i^α be a unit vector pointing along the long axis of molecule α, and form combinations with ν_i^α and δ_{ij}, $(\nu_{i_j}^\alpha \cdots \nu_{i_m}^\alpha)_s$, which are completely symmetric in all variables and traceless when any two indices are contracted. The two lowest-order combinations are

$$(\nu_i\nu_j)_s = \nu_i\nu_j - \tfrac{1}{3}\delta_{ij}$$

$$\begin{aligned}(\nu_i\nu_j\nu_k\nu_l)_s = \nu_i\nu_j\nu_k\nu_l &- \tfrac{1}{7}(\nu_i\nu_j\delta_{kl} + \nu_i\nu_k\delta_{jl} + \nu_i\nu_l\delta_{jk} \\ &+ \nu_j\nu_k\delta_{il} + \nu_j\nu_l\delta_{ik} + \nu_k\nu_l\delta_{ij}) \\ &+ \tfrac{1}{35}(\delta_{ij}\delta_{kl} + \delta_{il}\delta_{jk} + \delta_{ik}\delta_{jl})\,.\end{aligned} \qquad (3.6)$$

Tensor order parameters can then be introduced

$$\begin{aligned}\sigma^{nm}_{i_1\cdots i_{2m}} &= 2\rho_0 \frac{1}{N}\sum_\alpha \langle \cos n\vec{q}_0 \cdot \vec{r}^{\,\alpha}(\nu_{i_1}^\alpha \cdots \nu_{i_{2m}}^\alpha)_s\rangle \\ &= \sigma^{nm}(n_{i_1}\cdots n_{i_{2m}})_s\,,\end{aligned} \qquad (3.7)$$

where n_i is the familiar nematic director specifying the direction of preferred ordering. In smectic A's, $\vec{n}$ is parallel to $\vec{q}_0$. Note that σ^{01}_{ij} is simply related to the symmetric, traceless nematic order parameter:

$$\sigma^{01}_{ij} = 2\rho_0 Q_{ij} = 2\rho_0 \langle P_2 \rangle (n_i n_j - \tfrac{1}{3}\delta_{ij}) . \tag{3.8}$$

$f(\vec{r}, \Omega)$ can now be reexpressed as

$$f(\vec{r}, \Omega) = \frac{\rho_0}{4\pi} + \sum_{nm} \sigma^{nm}_{i_1 \cdots i_{2m}} \cos n(\vec{q}_0 \cdot \vec{r} + \phi) C^m_{i_1 \cdots i_{2m}}(\Omega) , \tag{3.9}$$

where

$$C^m_{i_1 \cdots i_{2m}} = \frac{4m+1}{4\pi} \frac{(4m)!}{2^{2m}(2m)!\,(2m)!} (\nu_{i_1} \cdots \nu_{i_{2m}})_s . \tag{3.10}$$

ν_i is a unit vector pointing in the direction of Ω. The Einstein convention is used on repeated subscripts. The prefactor in Eq. (3.10) insures that the normalization of Eqs. (3.3) and (3.4) is the same.

Finally, we introduce complex order parameters similar to $\tilde{\rho}_n$:

$$\tilde{\sigma}^{nm}_{i_1 \cdots i_{2m}} = \sigma^{nm}_{i_1 \cdots i_{2m}} e^{in\phi} . \tag{3.11}$$

The free energy must be invariant with respect to uniform rotations and uniform translations of the coordinate-system origin. The only combinations of $\tilde{\sigma}^{nm}_{i_1 \cdots i_{2m}}$ which satisfy these criteria are those which have no phase dependence and which have been fully contracted with respect to all Cartesian indices. Examples of acceptable invariant combinations are

$$\begin{aligned} &\sigma^{01}_{ij}\sigma^{01}_{ij} \sim \langle P_2 \rangle^2 , \\ &\sigma^{10}(\sigma^{10})^* \sim \rho_1^2 , \\ &\sigma^{11}_{ij}\sigma^{01}_{ij}(\sigma^{10})^* \sim \rho_1 \langle P_2 \rangle \sigma^{11} , \end{aligned} \tag{3.12}$$

and

$$\sigma^{11}_{ij}\sigma^{11}_{kl}\sigma^{02}_{ijkl}(\sigma^{20})^* \sim \rho_2 \langle P_4 \rangle (\sigma^{11})^2 .$$

Summation with respect to repeated indices is understood, and the exact coefficients on the right-hand side have not been calculated.

We are interested in the nematic to smectic-A transition. This transition is driven by the ordering field ρ_1. Our eventual aim must, therefore, be to obtain an effective free energy which is a function of ρ_1. To obtain this free energy, we start with a free energy expressed in terms of all variables which are zero in the nematic phase and nonzero in the smectic phase. We then eliminate all driven variables in favor of ρ_1, as ρ_2 was eliminated in Sec. II. All $\langle P_{2m} \rangle$'s are nonzero in the nematic phase whereas all σ^{nm}'s for $n > 0$ are zero. The $\langle P_{2m} \rangle$'s can undergo additional changes at the smectic transition. The initial free energy should, therefore, be expressed in terms of σ^{nm} ($n > 0$) and $\langle \delta P_{2m} \rangle$, the deviation of $\langle P_{2m} \rangle$ from its equilibrium value $\langle P_{2m} \rangle_0$ in the nematic phase. We would like to separate as much as possible those effects which result from orientational ordering from those which result from smectic positional ordering. To this end, we write

$$\sigma^{nm} = \rho_n \langle P_{2m} \rangle + \delta\sigma^{nm} \quad (m > 0) . \tag{3.13}$$

If nematic ordering is completely saturated (i.e., if the molecules do not fluctuate about their equilibrium orientation perpendicular to the smectic planes), $\delta\sigma^{nm}$ is zero and $\langle P_{2m} \rangle = 1$. We will express our initial free energy in terms of ρ_n, $\langle P_{2m} \rangle$, and $\delta\sigma^{nm}$ ($n, m > 0$).

The nonvanishing of $\langle P_{2m} \rangle$ in the nematic phase affects our analysis of the free energy in two important ways. First, all coefficients in the free energy can depend on $\langle P_{2m} \rangle_0$. Since all $\langle P_{2m} \rangle_0$'s for $m > 1$ are determined by $\langle P_2 \rangle_0$ within the simplest nematic mean-field theory (Meier-Saupe),[10] this means, in effect, that all coefficients depend on $\langle P_2 \rangle_0$. Second, the nematic equilibrium $\sigma^{0m}_{i_1 \cdots i_{2m}}$'s can be used to form invariant combinations with the variables $\tilde{\rho}_n$, $\delta\tilde{\sigma}^{0m}_{i_1 \cdots i_{2m}}$, and $\delta\tilde{\sigma}^{nm}_{i_1 \cdots i_{2m}}$ ($n, m > 0$). Hence, any combination of the latter variables which satisfies the phase constraint is an acceptable contribution to the free energy.

At the smectic transition, driven variables are proportional to some power of ρ_1. That power is equal to the power of ρ_1 appearing in the invariant combination of the driven variable and ρ_1 that is linear in the driven variable. For example, the following invariant combinations, linear in driven variables,

$$\begin{aligned} &\langle \delta P_{2m} \rangle \tilde{\rho}_1 \tilde{\rho}_1^* = \langle \delta P_{2m} \rangle \rho_1^2 , \\ &\delta\tilde{\sigma}^{2n}(\tilde{\rho}_1^*)^2 = \delta\sigma^{2n}\rho_1^2 , \\ &\delta\tilde{\sigma}^{1n}\tilde{\rho}_1^* = \delta\sigma^{1n}\rho_1 , \\ &\tilde{\rho}_n^*\tilde{\rho}_1^n = \rho_n \rho_1^n , \end{aligned} \tag{3.14}$$

imply that $\langle \delta P_{2m} \rangle$ and $\delta\sigma^{2n}$ are proportional to ρ_1^2, $\delta\sigma^{1n}$ to ρ_1, and ρ_n to ρ_1^n. We will assume that an expansion of the free energy to sixth power in ρ_1 is sufficient to describe the smectic-A to nematic transition. In this case, the coefficient of ρ_1^6 is positive, and the sign of the coefficient ρ_1^4 determines whether the transition is first or second order. In order to determine the coefficient of ρ_1^4 in the effective free energy, we start with a free energy that includes all terms up to order ρ_1^4. To keep expressions as compact as possible, we introduce a matrix notation.

Let

$$\underline{\delta\tau} = \begin{pmatrix} \langle \delta P_2 \rangle \\ \vdots \\ \langle \delta P_{2n} \rangle \\ \vdots \\ \delta\sigma^{21} \\ \vdots \\ \delta\sigma^{2n} \end{pmatrix}, \quad \underline{\delta\sigma}^1 = \begin{pmatrix} \delta\sigma^{11} \\ \vdots \\ \delta\sigma^{1n} \end{pmatrix}. \tag{3.15}$$

Then to fourth order in ρ_1, we have

$$F = \tfrac{1}{2}A_1\rho_1^2 + \tfrac{1}{2}A_2\rho_2^2 + \tfrac{1}{2}\underline{\delta\sigma}^{1T}\underline{C}^{-1}\underline{\delta\sigma}^1 + \tfrac{1}{2}\underline{\delta\tau}^T\underline{\chi}^{-1}\delta\vec{\tau} + \tfrac{1}{4}B_1\rho_1^4 - t\rho_1^2\rho_2 + \rho_1\underline{a}^T\underline{\delta\sigma}^1 + \rho_1^2\underline{b}^T\underline{\delta\tau} + \rho_1\underline{\delta\sigma}^{1T}\underline{I}\,\underline{\delta\tau}, \tag{3.16}$$

where $\underline{C}^{-1}$, $\underline{\chi}^{-1}$, and $\underline{I}$ are infinite dimensional coupling matrices, and $\underline{a}$ and $\underline{b}$ are infinite dimensional coupling vectors. $\underline{C}^{-1}$ and $\underline{\chi}^{-1}$ are positive definite; $\underline{I}$ is not a square matrix; it has two columns for every row. If nematic order is saturated, application of external fields will not enhance $\underline{\delta\tau}$ or $\underline{\delta\sigma}^1$. Hence both $\underline{C}$ and $\underline{\chi}$ become zero with saturated nematic ordering. The 11 component of χ is just the order-parameter susceptibility used by de Gennes in discussing this problem.[4] Minimization of F with respect to driven variables ρ_2, $\underline{\delta\tau}$, and $\underline{\delta\sigma}^1$ yields

$$F = \tfrac{1}{2}(A_1 - \underline{a}^T\underline{C}\,\underline{a})\rho_1^2 + \tfrac{1}{4}[B_1 - 2t^2/A_2 - 2(\underline{b}^T - \underline{a}^T\underline{C}\,\underline{I})\underline{\chi}\,(\underline{b} - \underline{I}^T\underline{C}\,\underline{a})]\rho_1^4. \tag{3.17}$$

Note that the coupling to $\underline{\delta\sigma}^1$ increases the nematic to smectic-A transition temperature from T_1^* to $T_{NA}^* = T_1^* + \underline{a}\,\underline{C}\underline{a}/a_1$ [cf. Eq. (2.6)]. Equation (3.17) shows that the coefficient of ρ_1^4 is reduced in magnitude by two types of terms. The first term results from coupling to the second Fourier component of the density and was discussed in Sec. II. Its effect is minimized by making $(T_{NA}^* - T_2^*)/T_{NA}^*$ as large as possible. The second term results from coupling parameters involving orientational order. Its effect is minimized by choosing systems with saturated nematic order at the smectic-A transition, i.e., by making T_{NI}/T_{NA} as large as possible where T_{NI} is the isotropic to nematic transition temperature.

IV. MOLECULAR-FIELD MODEL

The preceding analysis of the nematic-smectic-A transition is useful only near a second-order transition. For first-order transitions, or for temperatures far below T_{NA}, the power-series expansion of the free energy is inadequate. The simplest solution to this difficulty, within the mean-field theory, is to construct molecular models for the free energy of the ordered state which are functions of the ordering density, ignoring short-range correlation effects. The free energy so constructed can be minimized, usually by numerical methods, to determine the nature of the phase change and the temperature dependence of the order parameters. In this section, we will develop the usual molecular-field model, studied by Kirkwood and Monroe,[7] Kobayashi,[8] McMillan,[1,2] and Lee *et al.*,[9] for the case of saturated orientational ordering. We will then apply the results of Sec. III to locate the tricritical point in terms of model parameters.

For systems with saturated nematic ordering, an approximation to the potential energy for pairwise interactions is

$$E = \frac{1}{2}\iint d^3r\, d^3r'\, \rho(\vec{r})V(\vec{r} - \vec{r}')\rho(\vec{r}')g(\vec{r}, \vec{r}'), \tag{4.1}$$

in which $\rho(\vec{r})$ is the center-of-mass density introduced in Sec. II, $V(\vec{r} - \vec{r}')$ is the interparticle potential, and $g(\vec{r}, \vec{r}')$ is the pair correlation function. In the smectic phase, both ρ and g become periodic functions. However, following the mean-field approximation, we assume g is some fixed function only of $\vec{r} - \vec{r}'$ independent of the periodic structure of $\rho(\vec{r})$. Moreover, we assume that the period d of the smectic layers is known. If z is the axis normal to the smectic layers, since ρ is uniform in planes normal to z, we can immediately integrate E in the x and y dimensions. Then the internal energy density is

$$\epsilon = \frac{1}{2d}\int_0^d dz\, \rho(z)\int_{-\infty}^{+\infty} U(z - z')\rho(z')\, dz', \qquad U(z - z') = \int dx\, dy\, V(z - z', x, y)g(z - z', x, y). \tag{4.2}$$

Again ignoring local correlation effects, the contribution to the entropy density by the smectic ordering is

$$S = -\frac{k}{d}\int_0^d dz\, \rho(z)\ln\rho(z), \tag{4.3}$$

where k is Boltzman's constant.

The free-energy density is then $F = \epsilon - TS$. Expressed in terms of the Fourier components of $\rho(z)$, to order ρ_1^4, F is then

$$F \cong F_0 + \frac{k}{4\rho_0}(T - T_1^*)\rho_1^2 + \frac{kT}{32\rho_0^3}\rho_1^4 + \frac{k}{4\rho_0}(T - T_2^*)\rho_2^2 + \frac{kT}{32\rho_0^3}\rho_2^4 - \frac{kT}{8\rho_0^2}\rho_1^2\rho_2. \tag{4.4}$$

T_n^* is the unrenormalized ordering temperature for the nth Fourier component of the density:

$$T_n^* = -(\rho_0/k)U_n,$$
$$U_n = \int_0^\infty U(z)\cos(nq_0z)\,dz\,. \tag{4.5}$$

Using Eqs. (4.4) and (2.9), we obtain:

$$B_1'(T_1^*) = (kT_1^*/8\rho_0^3)[1 - T_1^*/2(T_1^* - T_2^*)]\,. \tag{4.6}$$

Hence, if $T_2^* < \frac{1}{2}T_1^*$, the transition is second order, and if $T_2^* > \frac{1}{2}T_1^*$, it is first order. The tricritical point occurs when $T_2^* = \frac{1}{2}T_1^*$. For monotonically varying $U(|z-z'|)$, this means that a deep narrow potential produces a first-order transition, while a broad flat potential leads to a second-order transition. For example, if U is a Gaussian,

$$U(z-z') = -U_0e^{-(z-z')^2/\lambda^2}\,. \tag{4.7}$$

Then

$$T_2^*/T_1^* = e^{-3\pi^2(\lambda/d)^2} \tag{4.8}$$

and the transition is second order if

$$\lambda/d > (\ln 2/3\pi^2)^{1/2} \cong \tfrac{1}{6}$$

This is reasonable. For a narrow potential, the smectic layers must be well ordered to lower the potential energy significantly. Therefore, a state with small order parameters will not be stable because it has too small an entropy. This results in a first-order transition. However, for a broad potential, a state with small order parameters lowers the potential energy enough to overcome the accompanying decrease in entropy. Such a state is therefore stable; i.e., a second-order transition is possible. The consequences of this model for determining the kind of molecule most likely to have a second-order transition will be discussed in Sec. VIII.

V. NUMERICAL METHODS FOR SATURATED NEMATIC ORDERING

In this section, we will continue to examine the molecular-field model for the free-energy density for the case of saturated nematic ordering. Instead of expanding F in a power series in the order parameters, one can attempt to minimize it with respect to variations of $\rho(z)$. Performing the variation of F subject to the constraint

$$\frac{1}{d}\int_0^d \rho(z)\,dz = \rho_0 \tag{5.1}$$

results in the Euler equation

$$\rho(z) = (\rho_0/A)e^{M(z)/kT},$$
$$A = \frac{1}{d}\int_0^d dz\, e^{M(z)/kT}, \tag{5.2}$$
$$M(z) = \int dz'\, U(z-z')\rho(z')\,.$$

A is a normalization constant. $M(z)$ is the mean potential experienced by a molecule at z due to the distribution of other molecules, $\rho(z')$.

Solving this equation requires approximate numerical methods. One approach is Fourier analyzing $\rho(z)$, which results in an infinite set of coupled integral equations for the order parameters, ρ_n:

$$\rho_n = \frac{2}{d}\int_0^d \rho(z)\cos(nq_0z)\,dz$$
$$= \frac{2}{Ad}\int_0^d \cos(nq_0z)e^{M(z)/kT}\,dz\,,$$
$$M(z) = \sum_n U_n\rho_n\cos(nq_0z)\,, \tag{5.3}$$
$$U_n = \int_0^\infty U(z)\cos(nq_0z)\,dz\,.$$

This set of equations can be truncated by truncating the potential at a finite wave vector, so that $U_n = 0$, for $n > n_0$. This results in a closed form for $M(z)$ involving only n_0 order parameters. Then only n_0 coupled equations need be solved to determine all order parameters.

One may be tempted to set $n_0 = 1$, to obtain the simplest result. This would be the analog, for smectic ordering, of the Meier-Saupe theory of nematic ordering.[10] For the nematic case, that approximation, using only the second Legendre polynomial in the pair potential, preserves the fundamental properties of the nematic-isotropic phase change, although it cannot give very accurate quantitative results. For the smectic case, this truncation sets $U_2 = 0$, and therefore $T_2^* = 0$. Therefore, it can produce only second-order nematic-smectic-A transitions. (We are considering now only the case of saturated nematic ordering.) Varying U_1 will merely change T_1^*. This is clearly an unacceptable approximation. One must work with $n_0 \geq 2$ to have first-order transitions.

A simpler numerical approach, not based on Fourier analysis, is the direct solution of the Euler equation (5.2) by an iterative method. Dividing the layer thickness into n equal intervals, with $\rho(z)$ approximated by the set $\rho(z_i)$ at the center of these intervals, the Euler equation becomes (for $\rho_0 = 1$ and length unit d/n)

$$\rho(z_i) = (1/A)e^{M(z_i)/kT}$$
$$A = \sum_i e^{M(z_i)/kT}, \tag{5.4}$$
$$M(z_i) = \sum_j \rho(z_j)U(z_i - z_j)\,.$$

This can be turned into an iteration scheme.

Starting with the mth estimate of $\rho(z_i)$, we generate the $(m+1)$th estimate as follows:

$$\begin{aligned} M^m(z_i) &= \sum_j \rho^m(z_j) U(z_i - z_j)\,, \\ R^m(z_i) &= e^{M^m(z_j)/kT} \\ A^m &= \sum_i R^m(z_i)\,, \\ \rho^{m+1}(z_i) &= R^m(z_i)/A^m\,. \end{aligned} \tag{5.5}$$

In practice, one must terminate $U(z_i - z_j)$ at some distance (N intervals) which can be as large as necessary.

This scheme was tried using $n = 20$ and $N = 40$. Using a PDP-10 computer programmed in FORTRAN, a single iteration, including a convergence test and all control processes, took about 3×10^{-2} sec of computing time.

The conditions for convergence of this algorithm were not examined in detail. For a Gaussian form of U, convergence was rapid and monotonic. For square wells, damped oscillations occurred at low temperatures, if one started from an initial $\rho(z)$ far from the equilibrium state. For potentials with a repulsive short-range part, undamped oscillation always occurred at low temperatures. The temperature for which oscillation first appeared depended on the detailed form of the potential; this phenomenon was not studied systematically. Probably convergence is assured for any potential with an absolute minimum at $z_i - z_j = 0$.

Convergence was determined by the criterion that the stepwise change of each ρ_i be less than some limit, typically 10^{-5} at low temperatures (below $0.9T_1^*$) and 10^{-7} or 10^{-8} at high temperatures. This stepwise criterion was tested by approaching the equilibrium state from higher and lower temperatures, i.e., from broader and narrower initial states. The agreement between the two $\rho(z)$ and sets of order parameters thus obtained was excellent; at worst, near the critical temperature, where convergence was slowest, the difference between the two sets of numbers was less than 100 times the convergence limit, while at low temperatures it was less than 10 times the convergence limit.

The dynamics of convergence mimicked critical behavior, qualitatively. At low temperatures, below $0.8T_1^*$, stepwise convergence to a limit of 10^{-7} took 5 to 30 iterations, depending on the initial state. Near a second-order transition, for a change of temperature from $0.998T_1^*$ to $0.999T_1^*$, several hundred iterations were required for the same convergence.

From the $\rho(z_i)$ and the potential U, the first five ρ_n and the free energy were calculated. Free energies were measured relative to the free energy of the disordered state (all $\rho_i = 1/n$) at the same T. The potential had initially been normalized so that $U_1 = -n$, which adjusts the temperature scale so that $kT_1^* = 1$.

The behavior of this model for various potentials was examined. In all cases, the behavior near the transition was that predicted by the Landau theory. For $U_2 < \frac{1}{2}U_1$, the transition was second order, occurring at $T = T_1^*$. For $U_2 > \frac{1}{2}U_1$ the transition was first order. In this case, near T_1^*, the program could converge to either one of two different minima in the free energy, one for all $\rho_i = 1/n$, and one for an ordered state, depending on the nature of the state from which iteration began. The equilibrium transition temperature could be located from the zero of the free energy of the ordered state. The transition entropy could be measured from the slope $\partial F/\partial T$ at this point.

Some results of the numerical calculations for continuous transitions are shown in Figs. 1–3. For a second-order transition far from the tricritical point, a comparison is made between a square-well potential of half-width $0.2d$, for which $T_2^*/T_1^* = 0.158\,38$, and a Gaussian potential of half-width $0.2495d$, which has the same value of T_2^*/T_1^*. In Fig. 1(a), we see that near T_c ($= T_1^*$), the order parameters approach zero with the power laws calculated from the Landau theory, for both potentials. Note also that ρ_1 and ρ_2 for the two potentials become identical in magnitude near T_c, as might be expected since T_2^*/T_1^* is the same for both potentials. However, ρ_3, ρ_4, and ρ_5, for the two potentials, differ in magnitude; in fact ρ_5 is negative for the square well.

In Fig. 2, the low-temperature behavior of the order parameters is easily compared. For the Gaussian potential, all order parameters rapidly approach one, indicating that the ground state is a δ-function density distribution. For the square-well potential the low-temperature behavior indicates that the ground state is not a δ-function density distribution, but is in fact a square distribution with a full width equal to the half-width of the potential. This ground state maximizes entropy without sacrificing potential energy; in this respect, the square well is a pathological case. In Figs. 3(a) and 3(b), we see another comparison of the temperature dependence of the density distributions for these two potentials. At $0.98T_c$ the two density distributions are essentially identical. At $0.8T_c$, there is a slight difference between the two, the Gaussian potential giving a sharper distribution. At lower temperatures, the square-well potential produces a distribution which rapidly approaches the square ground-state form, while

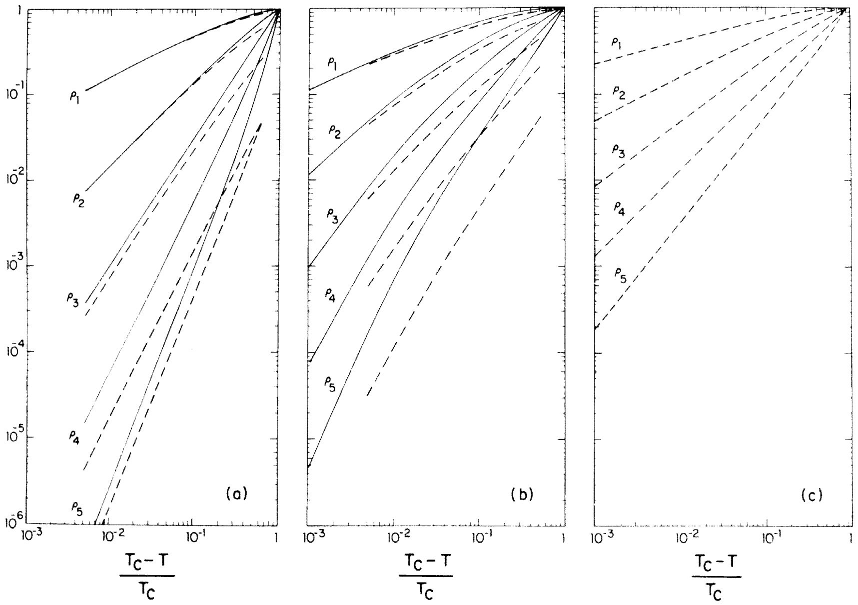


FIG. 1. Log-log plots of order parameters vs temperature for various potentials: (a) (---) square-well potential of half-width 0.2d, for which $T_2^*/T_1^* = 0.158\,38$. ρ_5 is negative. (——) Gaussian potential with the same T_2^*/T_1^*. (b) (---) square-well potential of half-width 0.15d, for which $T_2^*/T_1^* = 0.459\,65$. (——) Gaussian potential with the same T_2^*/T_1^*. (c) Tricritical transition, for a Gaussian potential.

the distribution due to the Gaussian rapidly sharpens.

One concludes that for a strongly second-order transition, the shape of the potential and the third- and higher-order parameters are irrelevant to determining the behavior near T_c; all that matters is T_2^*/T_1^*. In principle, the higher-order parameters indicate differences in the form of the potential, but they are probably always too small to measure accurately.

As the tricritical point is approached by changing T_2^*/T_1^*, the above conclusions apply over a progressively narrower temperature range. In Fig. 1(b), we see a comparison of order parameters for a square well of width 0.15d, for which $T_2^*/T_1^* = 0.459\,65$, and for the equivalent Gaussian potential. The range near T_c in which the Landau theory power laws for the order parameters are approached is smaller than in Fig. 1(a). Also, the magnitudes of ρ_1 and ρ_2 for the two potentials approach one another more slowly. The higher-order parameters are larger, and play a greater role in the behavior near the transition. In Fig. 1(c), the results for the tricritical Gaussian potential are shown. The tricritical power laws for the order parameters are obeyed. Comparing the data for the Gaussian potential in Fig. 1(b) with 1(c), we see the tendency for the crossover from tricritical power laws to second-order power laws beginning to be visible. A second-order transition closer to the tricritical point than the example in Fig. 1(b) would have shown this crossover more clearly. In Fig. 3(c), we see that the density distribution for the tricritical Gaussian potential remains distinctly peaked, nonsinusoidal, even very near T_c. The contribution from higher-order parameters remains significant.

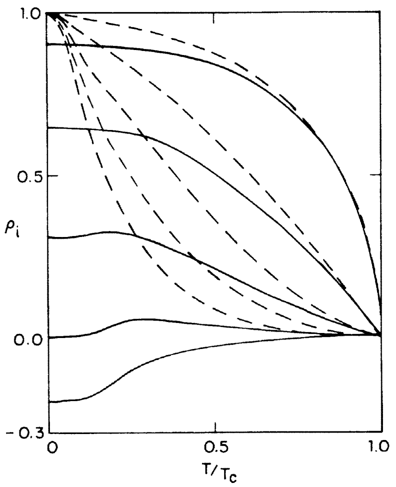


FIG. 2. Linear plots of order parameters vs temperature. (——) square-well potential of half-width 0.2d. (---) Gaussian potential with the same T_2^*/T_1^*.

For first-order transitions near the tricritical point, the order parameters change very rapidly near T_{NA}. The third- and higher-order parameters are surely no longer negligible in their effect on the transition, in the examples studied in these calculations. The Landau theory gives as a first approximation that ρ_n is proportional to ρ_1^n, for small order parameters. In Fig. 4, we test this prediction for a weakly first-order transition produced by a Gaussian potential of half-width

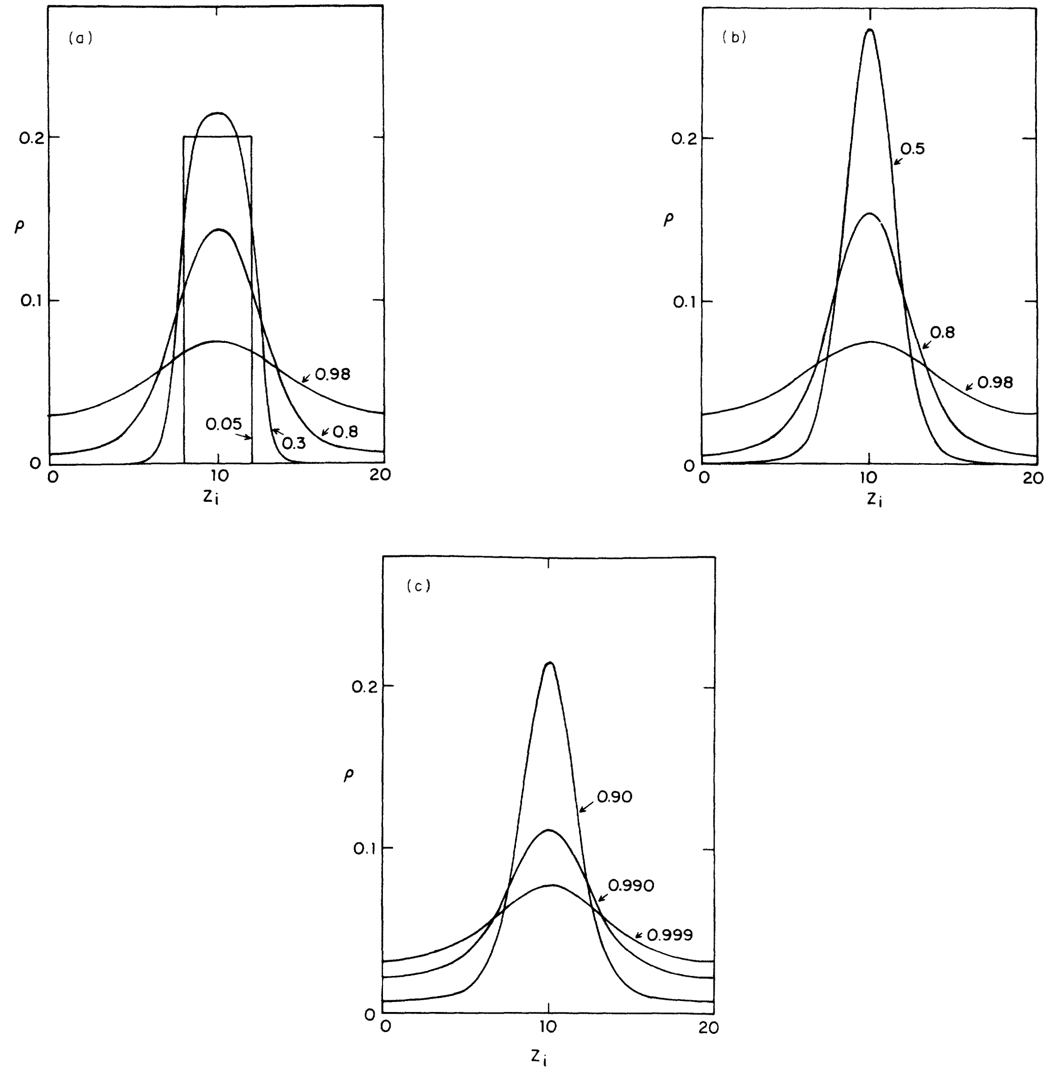


FIG. 3. Density distribution across a smectic layer, for different potentials, at reduced temperatures T/T_c, as labeled. The numerically calculated histograms as a function of z_i are represented by smooth curves. (a) Square-well potential of half-width $0.2d$. (b) Gaussian potential with the same T_2^*/T_1^*. (c) Tricritical Gaussian potential.

$0.14d$, for which $T_2^*/T_1^* = 0.5597$. Deviations from the simple-power-law relationship are evident. One concludes that detailed understanding of a first-order transition in which several order parameters are measurably large at T_{NA} would require careful modeling of the effective intermolecular interactions.

VI. NUMERICAL METHODS INVOLVING BOTH ORIENTATIONAL AND TRANSLATIONAL ORDERING

Having seen the effects of the coupling between ρ_1 and ρ_2 on the transition, and some of the behavior of the molecular-field model for saturated nematic ordering, it would be interesting to investigate the full orientational-translational molecular-field model for this transition. In fact, there have been several attempts to do this, reported in the literature, but they have been limited by the failure to recognize the importance of the coupling between ρ_1 and ρ_2 in determining the nature of the transition.

McMillan,[1,2] Kobayashi,[8] and Lee *et al.*[9] have considered mean-field theories of the nematic-smectic-A transition which start with a free-energy density

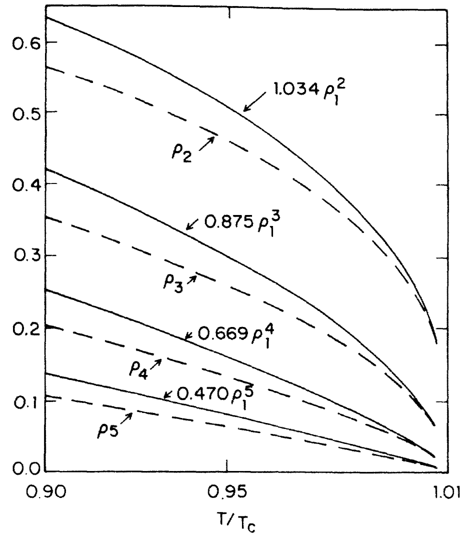


FIG. 4. Comparison of order parameters with powers of ρ_1 for a weakly first-order transition (Gaussian potential of half-width $0.14d$). To ease comparison, the powers of ρ_1 have been scaled to equal the respective order parameters at $T_{NA}=1.0062T_1^*$.

$$F=\frac{kT}{d}\int_0^d dz\int d\Omega f(z,\Omega)\ln 4\pi f(z,\Omega)$$
$$+\frac{1}{2d}\int_0^d dz\int d\Omega f(z,\Omega)\times\int dz'\int d\Omega'\,U(z-z',\Omega,\Omega')f(z'\Omega'),\tag{6.1}$$

in which

$$U(z-z',\Omega,\Omega')=\frac{-U_0}{\rho(\pi\lambda)^{1/2}}[P_2(\theta_{12})+\delta]\exp\left(\frac{-(z-z')^2}{\lambda^2}\right).\tag{6.2}$$

λ measures the interaction range, and δ determines the ratio of the orientation-independent part of the potential to the part which varies as $P_2(\theta_{12})$.

McMillan and Kobayashi both proceed by Fourier analyzing the problem and discarding all but the first translational Fourier component of the interaction. As discussed above, this immediately invalidates the quantitative results McMillan obtains for the location of the tricritical point, and for the temperature dependence of the order parameters in the smectic phase, because it artificially sets $T_2^*=0$, eliminating the influence of ρ_2 on the transition. All that remains to make the transition first order is the coupling of ρ_1 to the nematic ordering.

Lee *et al.* questioned McMillan's truncation of the interaction, and chose a safer method for approximately minimizing the free energy. They used a variational form of $f(z,\Omega)$:

$$f(z,\Omega)=(1/A)\exp\{\beta U_0[(a+b\cos q_0 z)P_2(\cos\theta_{12})+c\delta\cos q_0 z]\},\tag{6.3}$$

in which $\beta=1/kT$, A is a normalization constant, and a, b, and c are variational parameters. This form for F is similar to the form of the Euler equation, if we interpret the expression in square brackets as the mean potential $M(z,\Omega)$. It looks as if $M(z,\Omega)$ has been truncated after its first Fourier component. However, since this form for $f(z,\Omega)$ is now inserted in the full free-energy functional, which is then minimized to find a, b, and c, this approximation is not as bad as that of McMillan. However, it is not evident just how much of the interaction between ρ_1 and ρ_2 is preserved in this approach. It would have been much safer if $M(z,\Omega)$ had been truncated after two Fourier components, although even this is inadequate for strongly first-order transitions.

To determine accurately the second-order transition temperature, or to locate the tricritical point, for a general translational-orientational potential u, one could, in principle, use the general Landau-theory analysis described in Sec. III. This calculation, however, is impractical because it first requires a calculation of the orientational order parameters and their susceptibilities in the nematic phase just above T_{NA}. In other words, a complete understanding of the nematic phase is required before quantitative results for the nematic to smectic-*A* transition can be obtained.

A numerical approach to this problem could be based on the iterative scheme discussed in Sec. V. The extension to the full orientational-translational problem offers no fundamental difficulties. It would allow one to preserve properly the couplings between a large number of order parameters. In practice, of course, multidimensional computation schemes of this kind can use large amounts of computer time, compared to the one-dimensional case examined above. Therefore, although it would be interesting to try this calculation, it may not be justified until there are some reliable experimental data on both translational and orientational order parameters to be analyzed.

VII. POLAR SYSTEMS

Most liquid-crystal-forming molecules are not highly symmetric. For the nematic and smectic-*A* phases, it is not a bad approximation, for understanding many of their properties, to consider the molecules as cylindrical, rodlike objects. Because the molecules rotate relatively freely about their long axis, we will continue to consider them cylindrically symmetrical. However, if one end of the molecule is different from the other, we must pay attention to this polar asymmetry and its effects on the formation of smectic layers.

One can conceive of several ways for a smectic-*A* phase composed of polar molecules to be organized. The over-all symmetry of this phase dictates that it is not ferroelectric, so that there are equal numbers of molecules oriented in opposite directions. The "unit cell" could consist of two layers, with molecules all "up" in one layer, and all "down" in the next. Or all layers could be identical, with each containing equal numbers of "up" and "down" molecules. In that case, the layer thickness need not be simply the molecular length, since the two sets of molecules need not overlap perfectly. For several highly polar molecules (*p*-cyanobenzylidene-*p′*-octyloxyaniline and *p*-cyano′*p′*-octyloxybiphenzl, for instance) the layer thickness is on the order of 1.5 times the molecular length. The existence of such extreme cases clearly demands a model which accounts for molecular polarity. In this section, we will develop a simple mean-field model for such systems with saturated nematic ordering.

A. General considerations

For polar molecules, the center of mass is no longer a significant point of reference for describing intermolecular interactions or ordering. For now, we will choose a reference point within the molecule arbitrarily. In terms of this point, $\vec{r}^{\alpha}$ in molecule α, the densities of up (+) and down (−) molecules may be described as

$$\begin{aligned} \rho^+(\vec{r}) &= \left\langle \sum_\alpha \delta(\vec{r}-\vec{r}^{+\alpha})\right\rangle = \rho(\vec{r})+\epsilon(\vec{r}), \\ \rho^-(\vec{r}) &= \left\langle \sum_\alpha \delta(\vec{r}-\vec{r}^{-\alpha})\right\rangle = \rho(\vec{r})-\epsilon(\vec{r}). \end{aligned} \tag{7.1}$$

These densities are expressed as the sum of two components, ρ, which is symmetric about points of inversion symmetry in the layer structure, and ϵ, which is antisymmetric about these points. Choosing the origin at a center of symmetry requires that $\rho^+(\vec{r}) = \rho^-(-\vec{r})$.

Again expressing ρ^+ and ρ^- as Fourier series, we have

$$\begin{aligned} \rho^+(\vec{r}) &= \frac{\rho_0}{2} + \sum_{n>0}[\rho_n \cos n(\vec{q}_0\cdot\vec{r}+\phi) + \epsilon_n \sin n(\vec{q}_0\cdot\vec{r}+\phi)] \\ &= \frac{\rho_0}{2} + \frac{1}{2}\sum_{n>0}[(\rho_n - i\epsilon_n)e^{in\phi}e^{in\vec{q}_0\cdot\vec{r}} + \text{c.c.}], \\ \rho^-(\vec{r}) &= \frac{\rho_0}{2} + \sum_{n>0}[\rho_n \cos n(\vec{q}_0\cdot\vec{r}+\phi) - \epsilon_n \sin n(\vec{q}_0\cdot\vec{r}+\phi)] \\ &= \frac{\rho_0}{2} + \sum_{n>0}[(\rho_n + i\epsilon_n)e^{in\phi}e^{in\vec{q}_0\cdot\vec{r}} + \text{c.c.}]. \end{aligned} \tag{7.2}$$

The real Fourier components ρ_n of Eq. (2.2) have been replaced by complex numbers $\rho_n \pm i\epsilon_n$.

One can now perform a general Landau series expansion of the free-energy density in terms of the ρ_n and ϵ_n. Near a second-order transition, we expect terms quadratic in ρ_1 and ϵ_1 will be most important:

$$F \cong F_0 + \tfrac{1}{2}A_1\rho_1^2 + \tfrac{1}{2}\alpha_1\epsilon_1^2 - s\rho_1\epsilon_1 + \cdots. \tag{7.3}$$

Then, $\epsilon_1 \cong s\rho_1/\alpha_1$. Because ϵ_1 is linear in ρ_1, one could define a new order parameter which is a linear combination of ρ_1 and ϵ_1. In other words, we could choose the reference point within the molecule so that $s=0$ and ρ_1 is maximized in the ordered phase. This leaves ρ_1 the leading order parameter, and simplifies further development. ϵ_1 will now only develop as ρ_1^3 in the ordered phase. Note, however, that this choice of the molecular reference point only eliminates the $s\rho_1\epsilon_1$ term from the series. For $n>1$, ρ_n and ϵ_n are potentially of equal importance.

Retaining terms in F to order ρ_1^4

$$\begin{aligned} F = F_0 &+ \tfrac{1}{2}A_1\rho_1^2 + \tfrac{1}{4}B_1\rho_1^4 + \tfrac{1}{2}A_2\rho_2^2 + \tfrac{1}{2}\alpha_2\epsilon_2^2 \\ &- t\rho_1^2\rho_2 - v\rho_1^2\epsilon_2 + w\rho_2\epsilon_2 + \cdots. \end{aligned} \tag{7.4}$$

Minimizing F with respect to ρ_2 and ϵ_2, we find

$$\rho_2 \cong \frac{t\alpha_2 - wv}{\alpha_2 A_2 - w^2}\rho_1^2, \quad \epsilon \cong \frac{vA_2 - tw}{\alpha_2 A_2 - w^2}\rho_1^2, \tag{7.5}$$

$$F = F_0 + \tfrac{1}{2}A_1\rho_1^2 + \frac{1}{4}\left(B_1 - \frac{2\alpha_2 t^2 + 2A_2 v^2 - 4twv}{A_2\alpha_2 - w^2}\right)\rho_1^4. \tag{7.6}$$

Once again, the coupling of ρ_1 to ρ_2 and ϵ_2 tends to make the transition first order, by reducing the renormalized value of B_1. An estimate of the coefficients involved is made below.

B. Microscopic model

To develop the polar analog of the microscopic model for translational ordering discussed previously, we need to generalize the expression for the entropy and potential energy of the system. The entropy term in the free-energy density is

$$-TS = \frac{kT}{d}\int_0^d dz\,(\rho^+\ln\rho^+ + \rho^-\ln\rho^-). \tag{7.7}$$

The potential-energy density involves four potentials, to include all pairwise interactions between the two density components. The potentials between molecules of similar orientation are intrinsically symmetric, independent of the choice of reference point within the molecules:

$$U^{++} = U^{--} = \int dk\, U(k)\cos k(z_1 - z_2). \tag{7.8}$$

The potentials for molecules of opposite orientation can be divided into two parts, V and W, which are symmetric and antisymmetric, in terms of $z_1 - z_2$. With z_1 referring to the density component of the first superscript on U, we can Fourier analyze these two potentials as follows:

$$U^{+-} = \int dk[V(k)\cos k(z_1 - z_2) + W(k)\sin k(z_1 - z_2)]; \tag{7.9}$$

$$U^{-+} = \int dk[V(k)\cos k(z_1 - z_2) - W(k)\sin k(z_1 - z_2)].$$

The internal energy density is then

$$\overline{E} = \frac{1}{d}\int_0^d \int_{-\infty}^{\infty} dz_1\, dz_2[(\rho^+\rho^+ + \rho^-\rho^-)U^{++} + \rho^+\rho^-U^{+-} + \rho^-\rho^+U^{-+}]. \tag{7.10}$$

The Fourier analysis of $\overline{E}$ gives

$$\overline{E} = \frac{1}{2}\sum_n \{\rho_n^2[U(nq_0) + V(nq_0)] + \epsilon_n^2[U(nq_0) - V(nq_0)] + 2W(nq_0)\epsilon_n\rho_n\}. \tag{7.11}$$

Since the separation of U^{+-} and U^{-+} into V and W depends on the choice of reference points on the molecules, we can make $W(q_0) = 0$, which is equivalent to making $s = 0$ in the Landau expansion, and at the same time assume that $V(q_0)$ is negative. This means that the center of the smectic layer is nearer to the center of mass of the molecules than to their ends. We can now define transition temperatures for $\rho_n(T_n^*)$ and $\epsilon_n(T_n^0)$:

$$-kT_n^*/\rho_0 = U(nq_0) + V(nq_0);$$
$$-kT_n^0/\rho_0 = U(nq_0) - V(nq_0). \tag{7.12}$$

Since U and V are both attractive and of the same order of magnitude, then $T_1^* > T_1^0$, so that ρ_1 is the dominant order parameter at the transition.

Adding to these terms in the free-energy density those from the Fourier analysis of $-TS$, we can evaluate the terms of the Landau expansion above:

$$A_n = \frac{k}{\rho_0}(T - T_n^*), \quad \alpha_n = \frac{k}{\rho_0}(T - T_n^0), \quad B_n = kT/4\rho_0^3,$$
$$s = 0, \quad t = kT/4\rho_0^3, \quad v = 0, \quad w = W(2q_0)/\rho_0. \tag{7.13}$$

The renormalized value of B_1 at T_1^* is then

$$B_1'(T_1^*) = \frac{kT_1^*}{4\rho_0^3}\left(1 - \frac{T_1^*}{2\{T_1^* - T_2^* - [W(2q_0)]^2/k^2(T_1^* - T_2^0)\}}\right). \tag{7.14}$$

In the absence of the terms due solely to molecular polarity, this expression is identical to Eq. (4.6). Since $T_1^* - T_2^0 > 0$, if ρ_1 is the leading order parameter at the transition, "turning on" the polar interaction while keeping everything else the same tends to reduce $B_1'(T_1^*)$, making the transition more likely to be first order. Since T_2^0 and $W(2q_0)$ start from zero, when the polar interaction is turned on, this is only a second-order correction to B_1'. This is probably a small effect compared to the interaction between ρ_1 and ρ_2. One concludes that at least in terms of mean-field theory, molecular polarity is not evidently important. However, dipole-dipole interactions may have some specific effects on the intermolecular potential which are discussed below.

VIII. CONCLUSIONS AND DISCUSSION

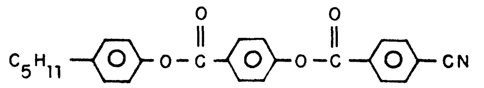
One of the fascinations of the nematic-smectic-A phase change is its variability from one material to another, in particular the fact that it may be first or second order. In this paper we have tried to explore the explanation of this variability in terms of the coupling of the dominant order parameter of the phase change to other order parameters. One of the major results of this investigation is the idea that coupling between the various translational order parameters, particularly the first and second, can be very important in determining the nature of the transition.

In Sec. II, the simplest calculation of this coupling was presented, and for the case of saturated nematic ordering, a criterion for first or second order, or tricritical, transitions was found. In Sec. III the general theory of coupling between different translational and orientational order parameters was developed, with the conclusion that a number of different couplings contribute to the determination of the first- or second-order nature of the transition. This raises the question of the relative importance in practice of these different couplings, and indicates that the most general approach to this problem requires extensive knowledge about both the nematic and the smectic phases near the transition.

In Sec. IV, the molecular-field model for saturated nematic ordering was used to estimate the magnitude of the coupling between the first and second translational order parameters, as a first step toward answering the question of the relative importance of different couplings. At the end of Sec. IV, a criterion for the tricritical point in terms of the width of the effective pair potential U was calculated. For the full width of the potential being greater than about one third of the layer spacing, the transition should be second order. If we interpret the width of the potential as roughly the length of the conjugated center section of the typical liquid-crystal molecule, and the layer spacing as roughly the total molecular length, this says that long molecular end chains promote a first-order nematic-smectic-A transition. This is the experimentally observed tendency.

In discussing the results of his model calculations, McMillan used the same interpretation of the width of the effective potential, relative to the layer spacing, and found the same tendency for a first-order transition to be promoted by long end chains. However, his calculations accounted for only the coupling between nematic and smectic ordering. One concludes that both kinds of coupling could be equally important. The question of their relative importance in reality remains open.

Experimental data should help clarify the situation. For instance, if materials are found for which the nematic ordering is saturated at the nematic-smectic-A transition, and that transition is first order, one can suspect that coupling between translational order parameters may be most important. An example is



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an asymmetric double benzoate, for which $T_{NI} = 249\,^{\circ}\mathrm{C}$ and $T_{NA} = 139\,^{\circ}\mathrm{C}$. With such a broad nematic range, nematic ordering is probably nearly complete at T_{NA}, but the transition to the smectic-A phase is first order.[11]

The minimal experimental data needed to resolve this kind of question are the magnitudes of the nematic, and at least the first two smectic order parameters near the transition, in addition to the basic thermodynamic data, including T_{NI}, T_{NA}, and the latent heat at T_{NA}. Even with these data, one must also make assumptions about some of the coefficients in the Landau theory, perhaps using those given by the molecular-field models for both the nematic and the smectic phases. Beyond this minimal combined experimental and theoretical effort to determine which couplings between order parameters tend to make this phase change first order, the prospect for more detailed understanding of this phase change remains unclear. On the experimental side, translational order parameters can be measured by x-ray or neutron scattering, and the first two orientational order parameters can be determined by various techniques, but the mixed nematic-smectic order parameters may be unmeasurable. On the theoretical side there is not a microscopic model for the coupling of orientational and translational order, so that even the simple theories considered here are rather incomplete.

The discussion of polar molecules was motivated by the existence of some highly polar liquid crystals which exhibit unusual properties in the smectic phase. The much studied CBOOA has a layer spacing roughly 1.5 times the molecular length and exhibits, probably, a second-order phase change. However, it may be that there is a strong tendency for CBOOA molecules to associate as pairs, oppositely oriented, and thus minimize the importance of the polarity of the individual molecules. In any case, our simple calculation did not indicate that polarity drives the transition second order; the opposite result is suggested. Polarity may have another effect not mentioned yet. Longitudinal dipole moments on neighboring molecules oriented parallel to one another, and perfectly ordered in layers, interact repulsively. If the molecules are slightly displaced from one another, in a direction normal to the layers, this repulsive interaction is eliminated, and at larger displacements the interaction is attractive. This adds a short-range repulsive interaction to the pair potential at $z_1 - z_2 = 0$, in this case. Note that in the case of an oppositely oriented pair of molecules, perfect layer ordering may place the dipole moments far from one another, so their interaction may be less important. This suggests that the presence of strong longitudinal dipole moments tends to broaden the normally attractive pair potential (U, in Sec. VII). This tends to decrease the ratio T_2^*/T_1^*, making the transition more likely to be second order. There is not enough experimental knowledge to test such a speculation.

The influence of other molecular interactions on this phase change remains to be explored. One important possibility is excluded-volume effects. The formalism of the molecular-field model discussed here can also be used for the lowest-order calculation of pairwise repulsive interactions, in the same spirit that this is done for the nematic phase.[12] Fundamentally, if molecules are ordered in noninterpenetrating layers, their freedom of motion within each layer is increased; smectic ordering can increase the entropy of the system by this mechanism. This model will be discussed in more detail elsewhere.

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