

Short-range correlations in two-dimensional liquid crystals.

II. Smectic and crystalline phases*

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A molecular theory of two-dimensional liquid crystals is developed. Taking short-range correlations explicitly into account, we show that in addition to isotropic and nematic phases, solutions representing smectic and crystalline phases can also be constructed as the number density increases beyond certain critical values. Relevant order parameters defined in a canonical ensemble are obtained as functions of density at fixed temperature.

I. INTRODUCTION

In an earlier paper,¹ based on work due to Kirkwood and Monroe² and more recently due to Brout³ and Jancovici,⁴ we developed a formalism which can be used to study the nature of short-range correlations and long-range order in liquid-crystal-like systems. In order to preserve a certain degree of simplicity, calculations were carried out in two dimensions and the isotropic-to-nematic phase transition was investigated. As a continuation of this effort we discuss in this paper transitions to smectic and crystalline phases.

From x-ray diffraction it is known that ordered phases of liquid crystals are characterized by density distributions appropriate to the symmetry of the phases, and are such that the order persists over macroscopic dimensions. On the other hand, the disordered phase shows only a rapidly damped local order about each molecule. We shall therefore identify the appearance of long-range order and each nonuniform density distribution of a definite symmetry with a phase transition. In different words, this means that order parameters suitably defined in a canonical ensemble will assume finite values with the onset of ordered phases; the details of which depend on the interaction potential and the particular transition under consideration.

Similar to well known methods in classical liquid⁵ we formulate integral equations for the distribution function $\rho(\vec{r}, \varphi)$ which specifies the average density of molecules at \vec{r} with orientation φ . The kernels of the integral equations will involve, apart from the interaction potential, a pair correlation function $g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2)$. This pair correlation function, which is set equal to unity in the usual mean field approximation, determines the local order in the density at \vec{r}_2 and along φ_2 relative to a molecule situated at \vec{r}_1 with orientation

φ_1 . We go beyond the mean field theory and obtain the required correlation function from approximate integral equations proven successful in the theory of classical liquids.

The major task begins with expanding $\rho(\vec{r}, \varphi)$ in a complete orthonormal set of functions appropriate to the symmetry of the problem. The integral equations for the density function can then be shown to reduce to a set of coupled transcendental equations which can be solved to obtain the coefficients of expansion. These coefficients are related to the relevant order parameters. It is found that for a given potential and a chosen temperature, the coefficients of expansion of $\rho(\vec{r}, \varphi)$ assume nontrivial values beyond a density which we can identify with the critical density for the phase transition. Each transition is characterized both by the critical density at which it appears and by the type of density distribution it takes up. Obviously the disordered, or isotropic, phase is represented by a constant $\rho(\vec{r}, \varphi)$ having complete translational and rotational symmetry.

There exist in the literature a number of papers⁶⁻¹⁰ on two-dimensional liquid-crystal-like systems. There are certain similarities between the results reported and ours, but it is difficult to make meaningful comparisons. For one thing, all of those calculations are on models featuring hard cores and no attraction. And also, the methods used were vastly different from ours—cluster expansion, scaled particle theory, Monte Carlo, etc.

II. THE MODEL

We consider a system of N molecules lying flat on a plane of area A and interacting through a pairwise potential $V(1, 2)$:

$$V(1, 2) = V(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) \\ = v_0(r_{12}) + v_2(r_{12}) \cos 2\varphi_{12}, \quad (1)$$

where $\vec{r}_i \equiv (x_i, y_i)$ denotes the position of the center of mass of the i th molecule, and φ_i gives its orientation. The angle φ_i is measured from the x axis. $r_{ij} \equiv |\vec{r}_i - \vec{r}_j|$ and $\varphi_{ij} \equiv |\varphi_i - \varphi_j|$. The thermodynamic limit

$$\lim_{N, A \rightarrow \infty} \left(\frac{N}{A} \right) = n$$

is assumed, and the average density n is taken to be an input parameter. To give a feeling of the order of magnitudes involved, we choose our parameters as follows¹:

$$v_0(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6], \quad (2)$$

$$v_2(r) = -\eta e^{-(r/r_0)^2}, \quad (3)$$

$$\sigma = 5 \text{ \AA}, \quad r_0 = 2\sigma = 10 \text{ \AA}, \quad (4)$$

$$\epsilon = 1.5532 \times 10^{-14} \text{ ergs}, \quad \epsilon/k_B = 112.5 \text{ K}, \quad (5)$$

$$\eta = 3.1644 \times 10^{-14} \text{ ergs}, \quad \eta/k_B = 229.2 \text{ K}, \quad (6)$$

$$T = 300 \text{ K}, \quad (7)$$

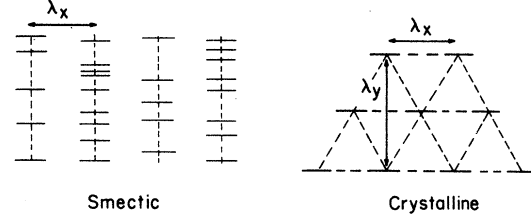
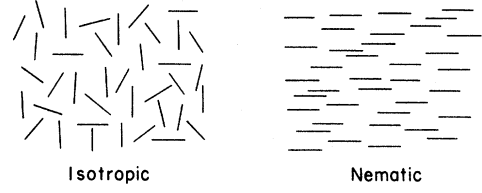


FIG. 1. Possible phases of the system.

where k_B is the Boltzmann constant and the fixed temperature T is taken to be roughly room temperature.

We wish to establish through this model the existence of the phases shown in Fig. 1.

III. INTEGRAL EQUATIONS FOR ONE-PARTICLE DISTRIBUTION FUNCTION

We define the ν -particle distribution function in the conventional manner⁵:

$$P^{(\nu)}(1, 2, \dots, \nu) = (2\pi)^\nu \frac{N!}{(N-\nu)!} \frac{\int_0^{2\pi} \int_A \exp[-(1/k_B T) \sum_{i < j} V(i, j)] d\varphi_{\nu+1} \cdots d\varphi_N d\vec{r}_{\nu+1} \cdots d\vec{r}_N}{\int_0^{2\pi} \int_A \exp[-(1/k_B T) \sum_{i < j} V(i, j)] d\varphi_1 \cdots d\varphi_N d\vec{r}_1 \cdots d\vec{r}_N}. \quad (8)$$

In particular we have the one- and two-particle distribution functions:

$$P^{(1)}(1) = 2\pi N \frac{\int_0^{2\pi} \int_A \exp[-(1/k_B T) \sum_{i < j} V(i, j)] d\varphi_2 \cdots d\varphi_N d\vec{r}_2 \cdots d\vec{r}_N}{\int_0^{2\pi} \int_A \exp[-(1/k_B T) \sum_{i < j} V(i, j)] d\varphi_1 \cdots d\varphi_N d\vec{r}_1 \cdots d\vec{r}_N} = n\rho(\vec{r}_1, \varphi_1) \quad (9)$$

and

$$P^{(2)}(1, 2) = (2\pi)^2 N(N-1) \frac{\int_0^{2\pi} \int_A \exp[-(1/k_B T) \sum_{i < j} V(i, j)] d\varphi_3 \cdots d\varphi_N d\vec{r}_3 \cdots d\vec{r}_N}{\int_0^{2\pi} \int_A \exp[-(1/k_B T) \sum_{i < j} V(i, j)] d\varphi_1 \cdots d\varphi_N d\vec{r}_1 \cdots d\vec{r}_N} \\ = n^2 \rho(\vec{r}_1, \varphi_1) \rho(\vec{r}_2, \varphi_2) g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) \quad (10)$$

where for convenience $(1, 2, \dots)$ is written to denote $(r_1, \varphi_1; r_2, \varphi_2; \dots)$. The functions

$$P^{(\nu)}(\vec{r}_1, \dots, \vec{r}_\nu) = \frac{1}{(2\pi)^\nu} \int_0^{2\pi} P^{(\nu)}(1, 2, \dots, \nu) d\varphi_1 \cdots d\varphi_\nu \quad (11)$$

and

$$P^{(\nu)}(\varphi_1, \dots, \varphi_\nu) = \frac{1}{A^\nu} \int_A P^{(\nu)}(1, 2, \dots, \nu) d\vec{r}_1 \cdots d\vec{r}_\nu \quad (12)$$

are ν -particle distribution functions defined respectively in the coordinate and the orientation space.

From Eq. (9) we obtain by taking derivatives two integrodifferential equations known as BGKY (Born-Green-Kirkwood-Yvon) equations⁵ for the one-particle distribution function. They are

$$-k_B T \frac{\partial}{\partial \varphi_1} \ln \rho(\vec{r}_1, \varphi_1) = \frac{n}{2\pi} \int_0^{2\pi} d\varphi_2 \int_A d\vec{r}_2 \rho(\vec{r}_2, \varphi_2) g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) v_2(r_{12}) \frac{\partial}{\partial \varphi_1} \cos 2\varphi_{12} \quad (13)$$

and

$$-k_B T \nabla_1 \ln \rho(\vec{r}_1, \varphi_1) = \frac{n}{2\pi} \int_0^{2\pi} d\varphi_2 \int_A d\vec{r}_2 \rho(\vec{r}_2, \varphi_2) g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) \nabla_1 [v_0(r_{12}) + v_2(r_{12}) \cos 2\varphi_{12}], \quad (14)$$

where we have made use of Eq. (1), and $\nabla_1 \equiv (\partial/\partial x_1, \partial/\partial y_1)$. We recognize that the above equations are nothing but equations for forces. The first of these expresses the torque due to the orientation-dependent part of the potential and the second the force due to the spatial parts. From Eqs. (13) and (14) we may deduce two equations for forces separately in the orientation and the coordinate space:

$$-k_B T \frac{1}{A} \int_A d\vec{r}_1 \frac{\partial}{\partial \varphi_1} \ln \rho(\vec{r}_1, \varphi_1) = \frac{n}{2\pi A} \int_0^{2\pi} d\varphi_2 \int_A d\vec{r}_1 \int_A d\vec{r}_2 \rho(\vec{r}_2, \varphi_2) g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) v_2(r_{12}) \frac{\partial}{\partial \varphi_1} \cos 2\varphi_{12} \quad (15)$$

and

$$-k_B T \frac{1}{2\pi} \int_0^{2\pi} d\varphi_1 \nabla_1 \ln \rho(\vec{r}_1, \varphi_1) = \frac{n}{(2\pi)^2} \int_0^{2\pi} d\varphi_2 \int_0^{2\pi} d\varphi_1 \int_A d\vec{r}_2 \rho(\vec{r}_2, \varphi_2) g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) \times \nabla_1 [v_0(r_{12}) + v_2(r_{12}) \cos 2\varphi_{12}]. \quad (16)$$

This procedure has the immediate advantage that it leads to a decoupling of Eqs. (13) and (14), retaining at the same time a simple physical interpretation. Equation (15) determines the orientational dependence of $\rho(\vec{r}, \varphi)$ due to the orientation part of the potential and an *average* spatial effect. On the other hand, Eq. (16) determines the spatial dependence of $\rho(\vec{r}, \varphi)$ due to the spatial part of the potential and an *average* orientational effect. From now on we shall consider Eqs. (15) and (16) instead of the pair (13) and (14) while fully recognizing that the decoupling represents an approximation which omits position-orientation corre-

lations.

The kernels of the integral equations (15) and (16) contain the yet unknown pair correlation function $g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2)$. In the next section we shall outline a method to determine $g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2)$.

IV. PAIR CORRELATION FUNCTION

As explained in Ref. 1, it is possible to obtain the following generalized Ornstein-Zernike equation relating the pair correlation function $g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2)$ to the direct correlation function $c(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2)$;

$$g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) - 1 = c(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) + \frac{n}{2\pi} \int_0^{2\pi} d\varphi_3 \int_A d\vec{r}_3 \rho(\vec{r}_3, \varphi_3) [g(\vec{r}_1, \varphi_1; \vec{r}_3, \varphi_3) - 1] c(\vec{r}_3, \varphi_3; \vec{r}_2, \varphi_2). \quad (17)$$

We can then use a generalized PY (Percus-Yevick) approximation to further connect $g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2)$ to $c(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2)$:

$$c(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) \approx g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) \times [1 - e^{V(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2)/k_B T}]. \quad (18)$$

Equations (15)–(18) form a closed set and can be solved self-consistently. This is a prohibitively difficult task and further approximations are necessary in order to render the problem numerically tractable.

We choose to neglect the difference between the short-range correlations in the disordered and ordered phases. This ansatz has been used before with a certain amount of success^{2,3} and leads to a tremendous amount of simplification. It implies that the information regarding long-range order can be lumped into the one-particle distribution function so that the pair correlation function retains only information regarding short-range, or local, order. Clearly such an approximation is

implied in the mean field theory where $g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2)$ is set equal to unity identically. Even then it works quite well.¹¹ Thus for the purpose of our paper we write

$$g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) \approx g_I(r_{12}; \varphi_{12}) \quad (19)$$

and

$$c(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) \approx c_I(r_{12}; \varphi_{12}) \quad (20)$$

where the subscript *I* stands for the isotropic phase (of a system made up of anisotropic molecules). Equations (17) and (18) then reduce to

$$g_I(r_{12}; \varphi_{12}) - 1 = c_I(r_{12}; \varphi_{12}) + \frac{n}{2\pi} \int_0^{2\pi} d\varphi_3 \int_A d\vec{r}_3 [g_I(r_{13}; \varphi_{13}) - 1] \times c_I(r_{32}; \varphi_{32}) \quad (21)$$

and

$$c_I(r_{12}; \varphi_{12}) = g_I(r_{12}; \varphi_{12}) [1 - e^{V(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2)/k_B T}]. \quad (22)$$

Thus for any input density n we solve the corresponding isotropic phase equation to obtain the pair correlation function.

Symmetry considerations, explained in Ref. 1, lead us to the following expansions

$$g_I(r_{12}; \varphi_{12}) = G_0(r_{12}) + 2 \sum_{m=1}^{\infty} G_{2m}(r_{12}) \cos 2m\varphi_{12} \quad (23)$$

and

$$c_I(r_{12}; \varphi_{12}) = c_0(r_{12}) + 2 \sum_{m=1}^{\infty} c_{2m}(r_{12}) \cos 2m\varphi_{12}. \quad (24)$$

Substitution of Eqs. (23) and (24) in Eq. (21) yields

$$G_0(r_{12}) - 1 = c_0(r_{12}) + n \int_A d\vec{r}_3 [G_0(r_{13}) - 1] c_0(r_{23}), \quad (25)$$

$$\gamma_0(r) g_0(\beta v_2(r)) + 2\gamma_2(r) g_1(\beta v_2(r)) = 1 + 2n \int_0^{\infty} s [\gamma_0(s) f_2(s) - 2\gamma_2(s) g_1(\beta v_2(s))] X(r, s) ds, \quad (27)$$

$$\gamma_0(r) g_0(\beta v_2(r)) + \gamma_2(r) [g_0(\beta v_2(r)) + g_2(\beta v_2(r))] = 2n \int_0^{\infty} s [\gamma_2(s) f_3(s) - \gamma_0(s) g_1(\beta v_2(s))] Y(r, s) \quad (28)$$

where β denotes $1/k_B T$, and

$$X(r, s) = \int_0^{\pi} \{ \gamma_0(|\vec{r} - \vec{s}|) [1 + f_1(|\vec{r} - \vec{s}|)] - 1 \} d\theta, \quad (29)$$

$$Y(r, s) = \int_0^{\pi} \gamma_2(|\vec{r} - \vec{s}|) [1 + f_1(|\vec{r} - \vec{s}|)] d\theta, \quad (30)$$

$$\gamma_0(r) = G_0(r) e^{\beta v_0(r)}, \quad \gamma_2(r) = G_2(r) e^{\beta v_0(r)}, \quad (31)$$

$$f_1(r) = e^{-\beta v_0(r)} - 1, \quad (32)$$

$$f_2(r) = e^{-\beta v_0(r)} - g_0(\beta v_2(r)), \quad (33)$$

$$f_3(r) = e^{-\beta v_0(r)} - g_0(\beta v_2(r)) - g_2(\beta v_2(r)), \quad (34)$$

$$g_m(a) = \frac{1}{2\pi i} \oint e^{(a/2)(t+1/t)} \frac{dt}{t^{m+1}}. \quad (35)$$

θ denotes the angle between \vec{r} and \vec{s} . Thus, for any given density n we solve Eqs. (27) and (28) obtaining $\gamma_0(r)$ and $\gamma_2(r)$, and from Eq. (31) the corresponding $G_0(r)$ and $G_2(r)$. At the end we have the truncated series

$$g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) \approx g_I(r_{12}, \varphi_{12}) \approx G_0(r_{12}) + 2G_2(r_{12}) \cos 2\varphi_{12}. \quad (36)$$

In the next section we shall use Eq. (36) to solve Eqs. (15) and (16) for $\rho(\vec{r}, \varphi)$.

V. SOLUTION OF EQUATIONS FOR ONE-PARTICLE DISTRIBUTION FUNCTION

As mentioned before, Eqs. (15) and (16) form a decoupled set. This suggests that their solution

$$G_{2m}(r_{12}) = c_{2m}(r_{12}) + n \int_A d\vec{r}_3 G_{2m}(r_{13}) c_{2m}(r_{23}), \quad m \neq 0. \quad (26)$$

We can then use Eqs. (23), (24), and (22) to obtain relationships between the coefficients $G_{2m}(r_{12})$ and $c_{2m}(r_{12})$ and rewrite Eqs. (25) and (26) in terms of $G_{2m}(r_{12})$ alone. This procedure gives rise to an infinite set of coupled nonlinear integral equations. As in Ref. 1, we retain only the first two terms of the expansions of $g_I(r_{12}; \varphi_{12})$ and $c_I(r_{12}, \varphi_{12})$. This reduces the infinite set to a set containing only two coupled nonlinear integral equations given below:

should be of the form

$$\rho(\vec{r}, \varphi) = \rho_T(\vec{r}) \rho_N(\varphi). \quad (37)$$

Recalling that $\rho(\vec{r}, \varphi)$ is a probability density, it seems as if the translational order is achieved completely independently of the orientation. Strictly speaking this is of course not true: The kernel of Eq. (16) contains an average effect of the orientational part. Similar arguments can be made for the orientational order. Based on Eq. (37), we write

$$\ln \Omega \rho(\vec{r}, \varphi) = 2 \sum_{m=1}^{\infty} \beta_{0,2m} \cos 2m\varphi + \sum_{\vec{k}=-\infty}^{+\infty} \beta'_{\vec{k},0} e^{i\vec{k} \cdot \vec{r}}, \quad (38)$$

where the constant term has been absorbed in the factor Ω which is to be determined from the normalization condition:

$$\frac{1}{2\pi\Delta} \int_{\Delta} d\vec{r} \int_0^{2\pi} d\varphi \rho(\vec{r}, \varphi) = 1. \quad (39)$$

In Eq. (38), \vec{k} represents the set of reciprocal-lattice vectors given by

$$\vec{k} \equiv (2\pi m/\lambda_x, 2\pi n/\lambda_y); \quad m, n = 0, \pm 1, \pm 2, \dots, \quad (40)$$

and the prime on the \vec{k} summation indicates the omission of $\vec{k} = 0$. Δ represents a unit cell. The expansion in φ is based on certain symmetry considerations explained earlier in Ref. 1. From Eqs. (38) and (39) we determine Ω ; thus

$$\Omega = \left[\frac{1}{2\pi} \int_0^{2\pi} \exp \left(2 \sum_{m=1}^{\infty} \beta_{0,2m} \cos 2m\varphi \right) d\varphi \right] \left[\frac{1}{\Delta} \int_{\Delta} d\vec{r} \exp \left(\sum_{\vec{k}} \beta'_{\vec{k},0} e^{i\vec{k} \cdot \vec{r}} \right) \right] = \Omega_N \Omega_T. \quad (41)$$

Then

$$\rho(\vec{r}, \varphi) = \rho_N(\varphi)\rho_T(\vec{r}) = \left[\frac{1}{\Omega_N} \exp\left(2 \sum_{m=1}^{\infty} \beta_{0,2m} \cos 2m\varphi\right) \right] \left[\frac{1}{\Omega_T} \exp\left(\sum_{\vec{k}}' \beta_{\vec{k},0} e^{i\vec{k}\cdot\vec{r}}\right) \right]. \quad (42)$$

For the sake of convenience we also make use of the expansion

$$\rho(\vec{r}, \varphi) = \alpha_{0,0} + 2 \sum_{m=1}^{\infty} \alpha_{0,2m} \cos 2m\varphi + \sum_{\vec{k}}' \alpha_{\vec{k},0} e^{i\vec{k}\cdot\vec{r}} + 2 \sum_{m=1}^{\infty} \sum_{\vec{k}}' \alpha_{\vec{k},2m} \cos 2m\varphi e^{i\vec{k}\cdot\vec{r}} \quad (43)$$

in intermediate steps of our derivation. Then, from Eqs. (42) and (43), we find

$$\alpha_{0,2m} = \frac{1}{2\pi\Omega_N} \int_0^{2\pi} \cos 2m\varphi \exp\left(2 \sum_{n=1}^{\infty} \beta_{0,2n} \cos 2n\varphi\right), \quad (44)$$

$$\alpha_{\vec{k},0} = \frac{1}{\Delta\Omega_T} \int_{\Delta} \exp\left(-i\vec{k}\cdot\vec{r} + \sum_{\vec{h}}' \beta_{\vec{h},0} e^{i\vec{h}\cdot\vec{r}}\right), \quad (45)$$

$$\alpha_{\vec{k},2m} = \alpha_{\vec{k},0} \alpha_{0,2m}. \quad (46)$$

Substitution of Eqs. (42), (43), and (36) in Eqs. (15) and (16) finally results in the following transcendental equations:

$$\beta_{\vec{k},0} = \omega_0(k) \alpha_{\vec{k},0} = \omega_0(k) \left[\int_{\Delta} d\vec{r} \exp\left(-i\vec{k}\cdot\vec{r} + \sum_{\vec{h}}' \beta_{\vec{h},0} e^{i\vec{h}\cdot\vec{r}}\right) / \int_{\Delta} d\vec{r} \exp\left(\sum_{\vec{h}}' \beta_{\vec{h},0} e^{i\vec{h}\cdot\vec{r}}\right) \right], \quad (47)$$

$$\beta_{0,2} = \frac{1}{2} \omega_2(0) \alpha_{0,2} = \frac{1}{2} \omega_2(0) \frac{\int_0^{2\pi} d\varphi \cos 2\varphi \exp(2\beta_{0,2} \cos 2\varphi + 2\beta_{0,4} \cos 4\varphi)}{\int_0^{2\pi} d\varphi \exp(2\beta_{0,2} \cos 2\varphi + 2\beta_{0,4} \cos 4\varphi)}, \quad (48)$$

$$\beta_{0,4} = \frac{1}{4} \omega_4(0) \alpha_{0,4} = \frac{1}{4} \omega_4(0) \frac{\int_0^{2\pi} d\varphi \cos 4\varphi \exp(2\beta_{0,2} \cos 2\varphi + 2\beta_{0,4} \cos 4\varphi)}{\int_0^{2\pi} d\varphi \exp(2\beta_{0,2} \cos 2\varphi + 2\beta_{0,4} \cos 4\varphi)}, \quad (49)$$

and $\beta_{0,6} = \beta_{0,8} = \dots = 0$. In the above,

$$\omega_0(k) = 2\pi \frac{n}{k_B T} \int_0^{\infty} \frac{J_1(kr)}{kr} \left(G_0(r) \frac{d}{dr} v_0(r) + G_2(r) \frac{d}{dr} v_2(r) \right) r^2 dr, \quad (50)$$

$$\omega_2(0) = -2\pi \frac{n}{k_B T} \int_0^{\infty} G_0(r) v_2(r) r dr, \quad (51)$$

$$\omega_4(0) = -2\pi \frac{n}{k_B T} \int_0^{\infty} G_2(r) v_2(r) r dr, \quad (52)$$

where $J_1(z)$ is the usual Bessel function of order 1. The solution of Eqs. (47)–(49) gives us complete information about the distribution function $\rho(\vec{r}, \varphi)$. However, it is evident that Eq. (47) forms an infinite set of coupled transcendental equations, and further truncation is necessary. If we assume that $\omega_0(k) = 0$ for $k > 2\pi(1/\lambda_x^2 + 1/\lambda_y^2)^{1/2}$, then it follows that $\beta_{\vec{k},0} = 0$ for $k > 2\pi(1/\lambda_x^2 + 1/\lambda_y^2)^{1/2}$. As remarked by Kirkwood and Monroe² the vanishing of the coefficients $\beta_{\vec{k},0}$ for $k > 2\pi(1/\lambda_x^2 + 1/\lambda_y^2)^{1/2}$ is due to the neglect of $\omega_0(k)$, and does not imply the vanishing of the corresponding coefficients $\alpha_{\vec{k},0}$. Numerical work shows that up to the density considered this assumption is very well justified. This then reduces the infinite set of transcendental equations to a set of only three:

$$\beta_{x,0} = \omega_0 \left(\frac{2\pi}{\lambda_x} \right) \frac{\int_0^{\lambda_x} dx \int_0^{\lambda_y} dy \cos(2\pi x/\lambda_x) f(\beta_{x,0}, \beta_{y,0}, \beta_{xy,0}; x, y)}{\int_0^{\lambda_x} dx \int_0^{\lambda_y} dy f(\beta_{x,0}, \beta_{y,0}, \beta_{xy,0}; x, y)}, \quad (53)$$

$$\beta_{y,0} = \omega_0 \left(\frac{2\pi}{\lambda_y} \right) \frac{\int_0^{\lambda_x} dx \int_0^{\lambda_y} dy \cos(2\pi y/\lambda_y) f(\beta_{x,0}, \beta_{y,0}, \beta_{xy,0}; x, y)}{\int_0^{\lambda_x} dx \int_0^{\lambda_y} dy f(\beta_{x,0}, \beta_{y,0}, \beta_{xy,0}; x, y)}, \quad (54)$$

$$\beta_{xy,0} = \omega_0 \left(2\pi \left(\frac{1}{\lambda_x^2} + \frac{1}{\lambda_y^2} \right)^{1/2} \right) \frac{\int_0^{\lambda_x} dx \int_0^{\lambda_y} dy \cos(2\pi x/\lambda_x) \cos(2\pi y/\lambda_y) f(\beta_{x,0}, \beta_{y,0}, \beta_{xy,0}; x, y)}{\int_0^{\lambda_x} dx \int_0^{\lambda_y} dy f(\beta_{x,0}, \beta_{y,0}, \beta_{xy,0}; x, y)}, \quad (55)$$

where

$$f(\beta_{x,0}, \beta_{y,0}, \beta_{xy,0}; x, y) = \exp\left(2\beta_{x,0} \cos \frac{2\pi x}{\lambda_x} + 2\beta_{y,0} \cos \frac{2\pi y}{\lambda_y} + 4\beta_{xy,0} \cos \frac{2\pi x}{\lambda_x} \cos \frac{2\pi y}{\lambda_y}\right). \quad (56)$$

In these derivations, we have clearly made use of the reflection symmetries of the lattice, namely,

$$\begin{aligned}\beta_{x,0} &\equiv \beta_{10,0} = \beta_{-10,0}, \\ \beta_{y,0} &\equiv \beta_{01,0} = \beta_{0-1,0}, \\ \beta_{xy,0} &\equiv \beta_{11,0} = \beta_{-1-1,0} = \beta_{1-1,0} = \beta_{-11,0}.\end{aligned}\quad (57)$$

Various order parameters are defined in the following way:

$$\begin{aligned}\tau_N^{(2)} &= \frac{1}{2\pi\Delta} \int_{\Delta} d\vec{r} \int_0^{2\pi} d\varphi \cos 2\varphi \rho(\vec{r}, \varphi) \\ &= \frac{1}{2\pi} \int_0^{2\pi} d\varphi \cos 2\varphi \rho_N(\varphi),\end{aligned}\quad (58)$$

$$\tau_N^{(4)} = \frac{1}{2\pi} \int_0^{2\pi} d\varphi \cos 4\varphi \rho_N(\varphi), \quad (59)$$

$$\begin{aligned}\tau_S &= \frac{1}{2\pi\Delta} \int_{\Delta} d\vec{r} \int_0^{2\pi} d\varphi \left\{ \begin{array}{l} \cos(2\pi x/\lambda_x) \\ \cos(2\pi y/\lambda_y) \end{array} \right\} \rho(\vec{r}, \varphi) \\ &= \frac{1}{\Delta} \int_{\Delta} d\vec{r} \left\{ \begin{array}{l} \cos(2\pi x/\lambda_x) \\ \cos(2\pi y/\lambda_y) \end{array} \right\} \rho_T(\vec{r}),\end{aligned}\quad (60)$$

and

$$\tau_X = \frac{1}{\Delta} \int_{\Delta} d\vec{r} \cos \frac{2\pi x}{\lambda_x} \cos \frac{2\pi y}{\lambda_y} \rho_T(\vec{r}). \quad (61)$$

Existence of these parameters implies the existence of corresponding phases with their characteristic distribution functions.

In summary at any given density we first solve the coupled integral equations (27) and (28) to obtain $G_0(r)$ and $G_2(r)$. The values of $G_0(r)$ and $G_2(r)$ are next used to evaluate $\omega_0(k)$, $\omega_2(0)$, and $\omega_4(0)$ from Eqs. (50), (51), and (52). This enables us to solve the set of Eqs. (48), (49), (53), (54), and (55), and use the results in Eq. (42) to find the distribution function $\rho(\vec{r}, \varphi)$. Finally, order parameters are calculated with the help of Eqs. (58)–(61). In this way we obtain the order parameters as function of density. An analysis of Eqs. (48), (49), (53), (54), and (55) shows that the following classes of solutions should exist.

Isotropic phase:

$$\beta_{x,0} = \beta_{y,0} = \beta_{xy,0} = 0 \quad \text{and} \quad \beta_{0,2} = \beta_{0,4} = 0.$$

This represents the solution $\rho(\vec{r}, \varphi) = 1$.

Nematic phase:

$$\beta_{x,0} = \beta_{y,0} = \beta_{xy,0} = 0 \quad \text{and} \quad \beta_{0,2} \neq 0, \quad \beta_{0,4} \neq 0.$$

This represents the solution

$$\rho(\vec{r}, \varphi) = \frac{1}{\Omega_N} \exp(2\beta_{0,2} \cos 2\varphi + 2\beta_{0,4} \cos 4\varphi). \quad (62)$$

The corresponding order parameters $\tau_N^{(2)}$ and $\tau_N^{(4)}$ are obtained from the numerical solution of the transcendental equations (48) and (49).

Smectic phase:

$$\beta_{x,0} \neq 0, \quad \beta_{y,0} = 0, \quad \beta_{xy,0} = 0 \quad \text{and} \quad \beta_{0,2} \neq 0, \quad \beta_{0,4} \neq 0.$$

(It is easy to see that there is also a similar solution with $\beta_{x,0} = 0$, $\beta_{y,0} \neq 0$.) To see that such a solution really exists, note that

$$\begin{aligned}\int_0^{\lambda_x} dx \int_0^{\lambda_y} dy \cos \frac{2\pi y}{\lambda_y} \exp\left(2\beta_{x,0} \cos \frac{2\pi x}{\lambda_x}\right) &= 0, \\ \int_0^{\lambda_x} dx \int_0^{\lambda_y} dy \cos \frac{2\pi y}{\lambda_y} \cos \frac{2\pi x}{\lambda_x} \\ &\times \exp\left(2\beta_{x,0} \cos \frac{2\pi x}{\lambda_x}\right) = 0.\end{aligned}\quad (63)$$

The distribution function is now given by

$$\begin{aligned}\rho(\vec{r}, \varphi) &= \frac{1}{\Omega_N} \exp(2\beta_{0,2} \cos 2\varphi + 2\beta_{0,4} \cos 4\varphi) \\ &\times \frac{1}{\Omega_S} \exp\left(2\beta_{x,0} \cos \frac{2\pi x}{\lambda_x}\right).\end{aligned}\quad (65)$$

The order parameters $\tau_N^{(2)}$ and $\tau_N^{(4)}$ are obtained in the same way from Eqs. (48) and (49), and τ_S is obtained from Eq. (53) which reduces to

$$\beta_{x,0} = \omega_0 \frac{2\pi}{\lambda_x} \frac{g_1(2\beta_{x,0})}{g_0(2\beta_{x,0})}, \quad (66)$$

and can be solved graphically. Note that the density n does not determine λ_x uniquely. We take that value of λ_x which maximizes $\omega_0(2\pi/\lambda_x)$. This in all cases turns out to be nearly the value for which the potential is minimum. In our case it is 5.6 Å within the limitation of numerical errors.

Crystalline phase:

$$\beta_{x,0} = 0, \quad \beta_{y,0} = 0, \quad \beta_{xy,0} \neq 0 \quad \text{and} \quad \beta_{0,2} \neq 0, \quad \beta_{0,4} \neq 0.$$

To see that this solution really exists, note that

$$\begin{aligned}\int_0^{\lambda_x} dx \int_0^{\lambda_y} dy \left\{ \begin{array}{l} \cos(2\pi x/\lambda_x) \\ \cos(2\pi y/\lambda_y) \end{array} \right\} \\ \times \exp\left(4\beta_{xy,0} \cos \frac{2\pi x}{\lambda_x} \cos \frac{2\pi y}{\lambda_y}\right) &= 0.\end{aligned}\quad (67)$$

The distribution function is then given by

$$\begin{aligned}\rho(\vec{r}, \varphi) &= \frac{1}{\Omega_N} \exp(2\beta_{0,2} \cos 2\varphi + 2\beta_{0,4} \cos 4\varphi) \\ &\times \frac{1}{\Omega_X} \exp\left(4\beta_{xy,0} \cos \frac{2\pi x}{\lambda_x} \cos \frac{2\pi y}{\lambda_y}\right).\end{aligned}\quad (68)$$

As before we obtain $\tau_N^{(2)}$ and $\tau_N^{(4)}$ from Eqs. (48)

and (49), and τ_x from the solution of Eq. (55) which reduces to

$$\beta_{xy,0} = \omega_0 \left(2\pi \left(\frac{1}{\lambda_x^2} + \frac{1}{\lambda_y^2} \right)^{1/2} \right) \frac{g_1(2\beta_{xy,0})}{g_0(2\beta_{xy,0})}, \quad (69)$$

with the help of the integration formula¹²

$$\int_0^{\pi/2} \cos[(\mu - \nu)\theta] g_{\mu+\nu}(2z \cos \theta) = \frac{1}{2} \pi g_\mu(z) g_\nu(z). \quad (70)$$

In this case the density n determines λ_x and λ_y . This point will be discussed further in the next section.

Finally we must mention that there should also be a solution of the form $\beta_{x,0} \neq 0$, $\beta_{y,0} \neq 0$, $\beta_{xy,0} \neq 0$ and $\beta_{0,2} \neq 0$, $\beta_{0,4} \neq 0$. Since this gives us no new physical information, we will omit it from our present discussion.

VI. NUMERICAL RESULTS

Equations (27) and (28) were solved numerically on a computer. The method used was iterative. Starting with the n th-guess functions γ_0^n and γ_2^n , we calculated the integrals appearing on the right-hand sides and then solved the resulting linear simultaneous equations to obtain new functions γ_0^{n+1} and γ_2^{n+1} . The $(n+1)$ th-guess functions were then obtained in the following way:

$$\gamma_0^{n+1} = m_0 \gamma_0^n + (1 - m_0) \gamma_0^n, \quad 0 < m_0 \leq 1, \quad (71)$$

$$\gamma_2^{n+1} = m_2 \gamma_2^n + (1 - m_2) \gamma_2^n, \quad 0 < m_2 \leq 1. \quad (72)$$

The iterations were continued until

$$|\gamma_0^{n+1} - \gamma_0^n| \leq 10^{-5}, \quad (73)$$

$$|\gamma_2^{n+1} - \gamma_2^n| \leq 10^{-5} \quad (74)$$

were satisfied for every single point. In this way $G_0(r)$ and $G_2(r)$ were obtained for 13 different densities between $n = 0.5/10^2 \text{ \AA}^{-2}$ and $n = 2.55/10^2 \text{ \AA}^{-2}$. The rate of convergence depends of course on how good the input guess is. At the lowest density we started off with a guess obtained from cluster expansion. m_0 and m_2 were chosen to stabilize the iteration process. At such low densities good convergence was obtained regardless of the values of m_0 and m_2 chosen. At higher densities, in order to assure convergence, the initial guess was taken to be the converged output of the previous, lower density. Even so, at the highest density $n = 2.55/10^2 \text{ \AA}^{-2}$ we had to use $m_0 = m_2 \leq 0.25$ in order to keep the iteration process stable. While it took only nine iterations for $n = 0.50/10^2 \text{ \AA}^{-2}$ to converge, at $n = 2.55/10^2 \text{ \AA}^{-2}$ 50 iterations were needed.

The r -grid had to be chosen in such a way that a point fell on the position of the potential mini-

mum. Since the integrands vanished fairly rapidly with distance the integrals were truncated at $r_{\max} = 6.16\sigma = 30.8 \text{ \AA}$. For $r_{\max} \leq r \leq 2r_{\max}$, we took $G_0(r) = G_0(r_{\max})$ and extrapolated $G_2(r)$ by curve fitting at every single iteration. This precaution was very important, especially at high densities where the calculation became precociously sensitive.

Two different grid sizes were chosen:

$$(i) \quad \Delta r = 0.05\sigma = 0.25 \text{ \AA}, \quad \Delta \theta = 0.07854, \\ r_{\max} = 30.8 \text{ \AA} = 6.16\sigma; \quad (75)$$

$$(ii) \quad \Delta r = 0.18\sigma = 0.90 \text{ \AA}, \quad \Delta \theta = 0.07854, \\ r_{\max} = 30.8 \text{ \AA} = 6.16\sigma. \quad (76)$$

The finer grid took up 12 times more computer time, while improving the accuracy by less than 1%. Consequently for most of our calculation grid-size (ii) was employed.

Figures 2-4 show $G_0(r)$ and $G_2(r)$ at three typical densities.

Equations (48) and (49) were solved numerically with the help of another iterative procedure. Substituting $2\beta_{x,0} = z$ we see that Eq. (66) can be re-written as

$$\frac{z}{2\omega_0(2\pi/\lambda_x)} = \frac{g_1(z)}{g_0(z)}. \quad (77)$$

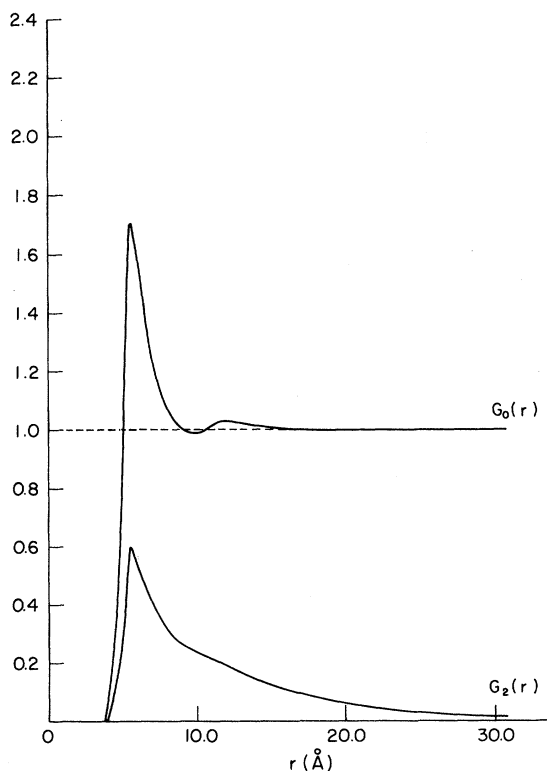
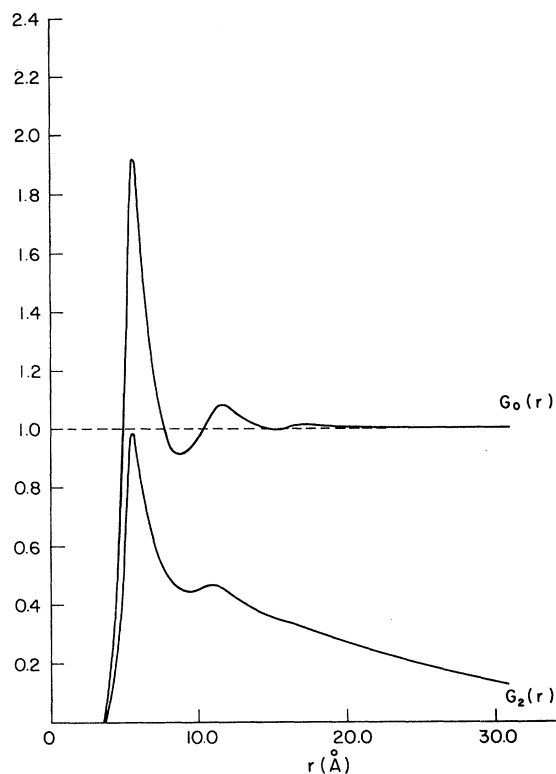
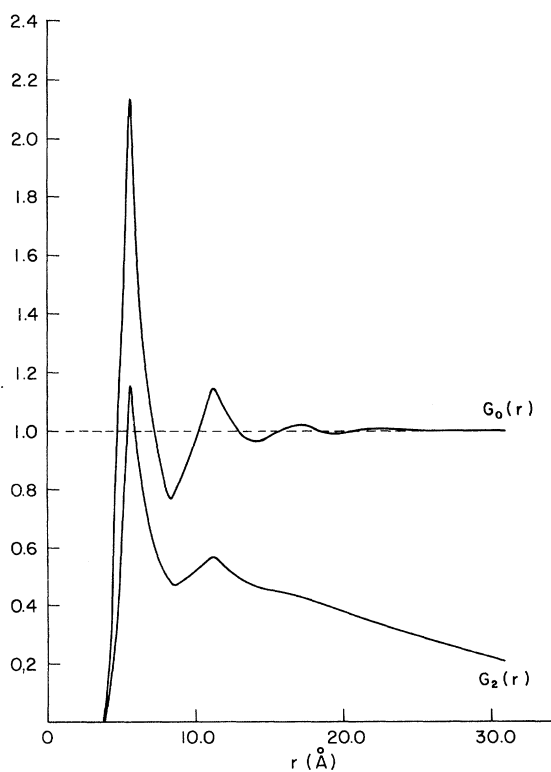


FIG. 2. $G_0(r)$ and $G_2(r)$ for $n = 0.70/10^2 \text{ \AA}^{-2}$.

FIG. 3. $G_0(r)$ and $G_2(r)$ for $n = 1.50/10^2 \text{ \AA}^{-2}$.FIG. 4. $G_0(r)$ and $G_2(r)$ for $n = 2.25/10^2 \text{ \AA}^{-2}$.

And since

$$\left. \frac{d}{dz} \left(\frac{g_1(z)}{g_0(z)} \right) \right|_{z=0} = \frac{1}{2} \quad (78)$$

by the recurrence properties of modified Bessel functions, a solution of Eq. (77) will exist if

$$\omega_0(2\pi/\lambda_x) \geq 1, \quad (79)$$

which can then be found graphically from the intersection of the straight line $f(z) = z/2\omega_0(2\pi/\lambda_x)$ with the curve $g_1(z)/g_0(z)$. Similar considerations applied to Eq. (69) lead to the condition for the existence of a solution of the latter in the form

$$\omega_0(2\pi(1/\lambda_x^2 + 1/\lambda_y^2)^{1/2}) \geq 1. \quad (80)$$

Thus we obtain all the order parameters as functions of density, as shown in Fig. 5.

For the crystalline phase we chose

$$\lambda_x = a, \quad \lambda_y = \sqrt{3} a, \quad (81)$$

so that the resulting lattice is made of equilateral triangles. The sides of each triangle is of length

$$a = (2/n\sqrt{3})^{1/2}. \quad (82)$$

VII. CONCLUSION

Based on the formalism due to Kirkwood and Monroe² and taking into account short-range correlations, we have been able to develop a theory which predicts liquid-crystal-like phase transitions for systems composed of anisotropic molecules. We have shown by examining a prototype problem in two dimensions that the relevant order parameters can be obtained in a natural way. As stated in our earlier paper,¹ we realize that phase transitions in two dimensions have intriguing im-

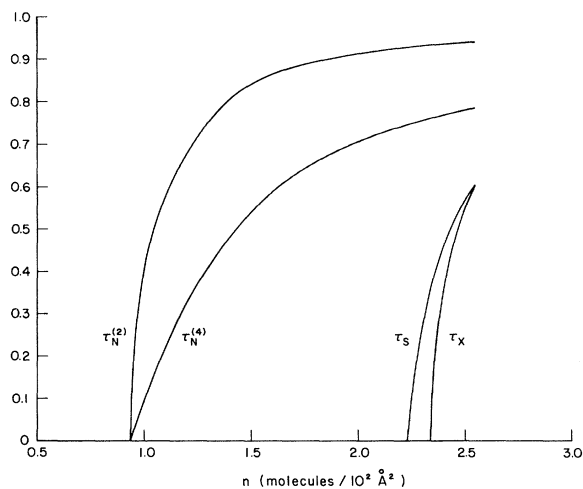


FIG. 5. Order parameters as functions of density.

plications¹³ in rigorous statistical-mechanical theories. Our work is clearly not sufficiently exact to make any significant statement regarding those fundamental questions. Further work re-

lating to measurable thermodynamic properties of liquid crystals must be performed on more realistic three-dimensional models. It is there that the ultimate test of our theory will be met.

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