

Short-range correlations in two-dimensional liquid crystals*

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We propose here a molecular theory of liquid crystals based on well-known theory of classical liquids. The method of calculation involves the simultaneous solution of two coupled nonlinear integral equations. The one- and two-particle distribution functions are obtained, as are order parameters as functions of density and temperature. The results are compared with those of mean-field calculations.

I. INTRODUCTION

In recent years there has been much interest and research activity centered upon the study of liquid crystals. However, despite encouraging progress made along the lines of mean-field theory¹⁻³ and hard-rod model calculations,⁴⁻⁷ a detailed and realistic microscopic theory of liquid crystals is still lacking.

In the mean-field approximation, short-range correlations between molecules are ignored, or at best accounted for in the crudest manner. While phase diagrams for homologous series can be obtained, in fact rather successfully, properties which depend on the pressure of the system cannot be accounted for. Yet some of the most interesting recent experiments are related in one way or another to this thermodynamic variable: the pressure. For example, there are now available *PVT* data for individual members of a homologous series^{8,9}; there are measurements of elastic constants¹⁰; and there are direct observations on sound propagation properties.^{11,12} Furthermore, neutron scattering experiments¹³ now provide a sensitive probe of microscopic structure functions. To understand and predict these important properties of liquid crystals one must move beyond the mean-field approximation.

Hard-core model calculations do take into consideration short-range intermolecular correlations. However, in these models there is too much emphasis on geometrical or steric effects. In reality, the intermolecular potentials are expected to be much softer and of multipolar nature. To bridge the gap between powerful but qualitative statistical-mechanical calculations and quantitatively accurate data obtained from experimentation on real-life liquid crystals, one must allow potentials of rather general forms into the microscopic theory.

In this paper, we propose a molecular theory of liquid crystals based on well-known theories of classical liquids. Undoubtedly, approximations of

various sorts are present, as will be made clear in the following pages. What we provide here is merely the first step in a strenuous journey. In subsequent papers we shall deal with applications of the formalism developed here, and attempt to link up with the available phenomenological, hydrodynamic theories.¹⁴⁻¹⁹ To illustrate how quantitative results can be produced from our theory, some simple numerical calculations are carried out for two-dimensional systems. The choice of dimensionality is merely for expediency. We realize that phase transitions in two dimensions have intriguing implications in rigorous statistical-mechanical theories. Our theory is clearly not sufficiently exact to make any significant statement regarding these fundamental questions. We are satisfied with the fact that order-disorder transitions in two dimensions are not ruled out by exact theories, the prime example of which being the well-known Ising model. The success or failure of our theory will rest on how well the three-dimensional version eventually fares when tested against empirical data.

In the given context, then, what is the most convenient way of representing an order-disorder transition? This question was answered a long time ago by Kirkwood and Monroe.²⁰ The one-particle distribution function becomes extremely important when one examines systems with long-range order. For example, as a liquid condenses into its solid phase, the one-particle distribution function goes over from a constant to one having periodic peaks situated on the lattice sites. Again, in the present case, as an isotropic liquid undergoes a transition into a nematic phase, the one-particle distribution function exhibits a sharp maximum along some preferred direction: that of the *director*. In both examples, we face the following theoretical difficulty: The only input happens to be the intermolecular potential. If this potential has a symmetry corresponding to that of the disordered phase, the transition to the ordered phase

represents a lowering of the symmetry. A one-particle distribution function naively defined in the usual canonical ensemble theory leads to complexities. If the potential is rotationally invariant, the one-particle distribution function is apparently a constant in either the isotropic or the nematic phase. One might simply accept this statement and proceed to look for order in the two-particle distribution function. Or alternately, one might introduce an arbitrarily weak single-particle field—one that furnishes a preferred axis in space and yet is too weak to affect otherwise the properties of the system. The latter approach, which we shall adopt in this paper, breaks the symmetry and selects the proper ensemble. The fictitious single-particle field will not explicitly appear in the equations; its presence will be tacitly assumed.

Let us then consider a system composed of N molecules confined to a plane of area A such that the limit $N/A \equiv n$ exists as N and A approach infinity. n is finite and an input parameter. The interaction is assumed to be pairwise. To be more specific, we shall take it in the following form:

$$v(1, 2) \equiv v(r_1, \phi_1; r_2, \phi_2) \\ = v_0(r_{12}) + v_2(r_{12}) \cos 2\phi_{12}, \quad (1)$$

where $\vec{r}_i \equiv (x_i, y_i)$ gives the position of the center of mass of the i th molecule, and ϕ_i gives its orientation. $r_{ij} \equiv |\vec{r}_i - \vec{r}_j|$; and $\phi_{12} = \phi_1 - \phi_2$. Figure 1 shows the geometry of a pair of molecules.

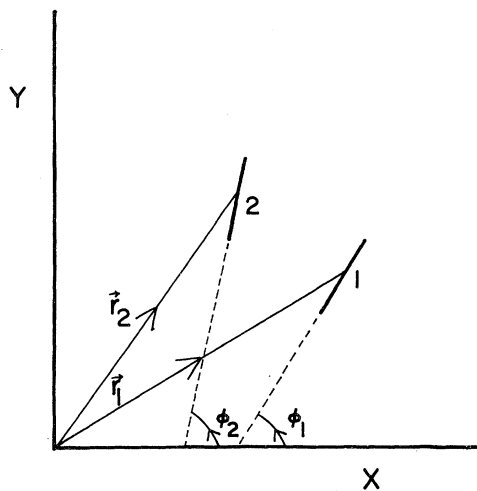


FIG. 1. Geometry of a pair of molecules. A molecule is represented by its symmetry axis.

$v_0(r)$ and $v_2(r)$ are functions to be constructed to make v as realistic as possible. Clearly one can, and perhaps eventually needs to, generate potentials which are more sophisticated than that given in Eq. (1); e.g., by including higher-order terms in cosines such as $\cos 4\phi_{12}$, etc. But such a move will only complicate the issue and adds nothing substantial to our present effort toward developing the theory. Also, it is possible to include odd cosine terms such as $\cos \phi_{12}$, etc. This destroys the two-fold symmetry of the rodlike molecule (with respect to a rotation by π), a property which is rather nice to ascribe to the molecules at this early stage of our research. For the numerical work in this paper, we take $v_0(r)$ to be of the popular Lennard-Jones form,

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

and $v_2(r)$ a Gaussian as in Refs. 2 and 3,

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

The values of the parameters ϵ , σ , η , and r_0 will be given later. Figure 2 shows qualitatively the angular and spatial dependence of such a pairwise potential.

II. DISTRIBUTION FUNCTIONS

We define the ν -particle distribution function in the conventional manner²¹:

$$P^{(\nu)}(1, 2, \dots, \nu) = \frac{N(N-1) \cdots (N-\nu+1)(2\pi)^\nu \int_0^{2\pi} \cdots \int_A \cdots \exp[-\beta \sum_{i < j} v(i, j)] dr_{\nu+1} \cdots dr_N d\phi_{\nu+1} \cdots d\phi_N}{\int_0^{2\pi} \cdots \int_A \cdots \exp[-\beta \sum_{i < j} v(i, j)] dr_1 \cdots dr_N d\phi_1 \cdots d\phi_N}. \quad (4)$$

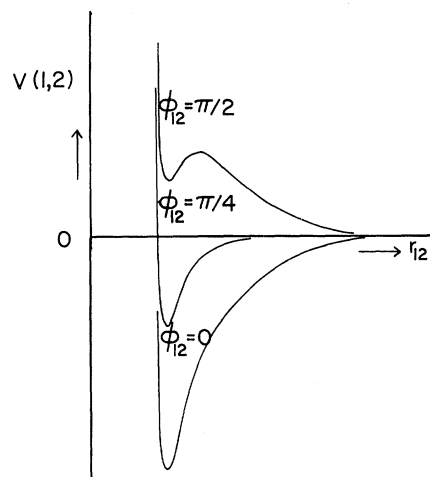


FIG. 2. Qualitative nature of the angular and spatial dependence of the interaction potential $V(1, 2)$.

For systems characterized by pairwise interactions the essential distribution functions are the one- and two-particle distribution functions

$$P^{(1)}(1) \equiv n\rho(r_1, \varphi_1) = N(2\pi) \frac{\int_0^{2\pi} \cdots \int_A \cdots \exp[-\beta \sum_{i < j} v(i, j)] d\vec{r}_2 \cdots d\vec{r}_N d\varphi_2 \cdots d\varphi_N}{\int_0^{2\pi} \cdots \int_A \cdots \exp[-\beta \sum_{i < j} v(i, j)] d\vec{r}_1 \cdots d\vec{r}_N d\varphi_1 \cdots d\varphi_N} \quad (5)$$

and

$$P^{(2)}(1, 2) \equiv n^2 \rho(\vec{r}_1, \varphi_1) \rho(\vec{r}_2, \varphi_2) g(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) \\ = N(N-1)(2\pi)^2 \frac{\int_0^{2\pi} \cdots \int_A \cdots \exp[-\beta \sum_{i < j} v(i, j)] d\vec{r}_3 \cdots d\vec{r}_N d\varphi_3 \cdots d\varphi_N}{\int_0^{2\pi} \cdots \int_A \cdots \exp[-\beta \sum_{i < j} v(i, j)] d\vec{r}_1 \cdots d\vec{r}_N d\varphi_1 \cdots d\varphi_N} \quad (6)$$

By restricting our present considerations to isotropic and nematic phases, both of which possess translational invariance, we find the "density" $\rho(\vec{r}, \varphi)$ depending only on the orientation φ and the "pair correlation function" $g(r_{12}, \varphi_1, \varphi_2)$ depending only on the magnitude of the distance r_{12} , and φ_1 and φ_2 . Thus we write

$$P^{(1)}(1) = n\rho(\varphi_1) \quad (7)$$

and

$$P^{(2)}(1, 2) = n^2 \rho(\varphi_1) \rho(\varphi_2) g(r_{12}; \varphi_1, \varphi_2). \quad (8)$$

Let us reiterate these facts and further inspect other properties of the system: symmetry, asymptotic behavior, and normalization. From these properties we wish to obtain infinite series in which these functions can be conveniently expanded.

For the density, we note the following: (i) It is a constant in the isotropic phase. In the nematic phase, once the rotational symmetry has been broken by the specification of the x axis from which one measures φ , the density becomes dependent on the orientation of the molecule but not the position of its center of mass. (ii) It is an even function of φ ; i.e., $\rho(\varphi) = \rho(-\varphi)$. (iii) It is invariant with respect to a rotation by π : $\varphi \rightarrow \varphi + \pi$. In other words, the molecules possess twofold rotational symmetry. (iv) It satisfies the normalization condition

$$\frac{1}{2\pi} \int_0^{2\pi} \rho(\varphi) d\varphi = 1. \quad (9)$$

For the pair correlation function, we observe the following: (i) $g(r_{12}; \varphi_1, \varphi_2)$ is a function of the relative distance between the centers of mass of the two molecules 1 and 2. (ii) $P^{(2)}(r_1, \varphi_1; r_2, \varphi_2)$ is symmetric with respect to an interchange of 1 and 2. This implies

$$g(r_{12}; \varphi_1, \varphi_2) = g(r_{21}; \varphi_2, \varphi_1). \quad (10)$$

(iii)

$$g(r_{12}; \varphi_1, \varphi_2) = g(r_{12}; -\varphi_1, -\varphi_2). \quad (11)$$

(iv) $g(r_{12}; \varphi_1, \varphi_2)$ is invariant with respect to the following transformations:

$$\varphi_1 \rightarrow \varphi_1 + \pi, \quad \varphi_2 \rightarrow \varphi_2 + \pi,$$

$$\varphi_1 \rightarrow \varphi_1 + \pi \quad \text{and} \quad \varphi_2 \rightarrow \varphi_2 + \pi.$$

(v) $g(r_{12}; \varphi_1, \varphi_2)$ approaches unity asymptotically; i.e.,

$$\lim_{r \rightarrow \infty} g(r; \varphi_1, \varphi_2) = 1. \quad (12)$$

(vi) $g(r_{12}; \varphi_1, \varphi_2)$ is a real function of its arguments.

These considerations lead first to the expansion of the density:

$$\rho(\varphi) = \sum_{m=0}^{\infty} a_{2m} \cos 2m\varphi, \quad (13)$$

where

$$a_0 = 1, \quad (14)$$

and

$$a_{2m} = (1/\pi) \int_0^{2\pi} \rho(\varphi) \cos 2m\varphi d\varphi. \quad (15)$$

The coefficients a_{2m} define the order parameters, as evidenced by a straightforward calculation of the latter (τ_{2m}) in terms of the usual thermal averages:

$$\tau_{2m} \equiv \lim_{N \rightarrow \infty} \frac{1}{N} \left\langle \sum_{i=1}^N \cos 2m\varphi_i \right\rangle \\ = \frac{1}{2} a_{2m}, \quad m \neq 0 \quad (16)$$

where

$$\langle \theta \rangle \equiv \frac{\int_0^{2\pi} \cdots \int_A \cdots \theta \exp[-(1/kT) \sum_{i < j} v(i, j)] d\vec{r}_1 \cdots d\vec{r}_N d\varphi_1 \cdots d\varphi_N}{\int_0^{2\pi} \cdots \int_A \cdots \exp[-(1/kT) \sum_{i < j} v(i, j)] d\vec{r}_1 \cdots d\vec{r}_N d\varphi_1 \cdots d\varphi_N} \quad (17)$$

Next we have the expansion of the pair correlation function:

$$g(r_{12}; \varphi_1, \varphi_2) = G_0(r_{12}) + 2 \sum_{m=1}^{\infty} G_{2,m}(r_{12}) \cos 2m\varphi_{12} \\ + 2 \sum_{m=1}^{\infty} G_m(r_{12}) (\cos 2m\varphi_1 + \cos 2m\varphi_2) + 2 \sum_{m=1}^{\infty} G'_m(r_{12}) \cos 2m(\varphi_1 + \varphi_2). \quad (18)$$

For an isotropic liquid, $g(r_{12}; \varphi_1, \varphi_2)$ is invariant with respect to a simultaneous rotation of the molecules; i.e., $\varphi_1 \rightarrow \varphi_1 + \alpha$ and $\varphi_2 \rightarrow \varphi_2 + \alpha$, where α is arbitrary. Under this condition, the terms involving $G_m(r_{12})$ and $G'_m(r_{12})$ drop out. Equation (18) reduces to

$$g(r_{12}; \varphi_{12}) = G_0(r_{12}) + 2 \sum_{m=1}^{\infty} G_{2,m}(r_{12}) \cos 2m\varphi_{12} \quad (19)$$

$$\equiv G_0(r_{12}) + 2G_2(r_{12}) \cos 2\varphi_{12} \\ + 2 \sum_{m=2}^{\infty} G_{2,m}(r_{12}) \cos 2m\varphi_{12}. \quad (20)$$

III. INTEGRAL EQUATIONS FOR THE DISTRIBUTION FUNCTIONS

It is well known²¹ from the theory of classical liquids that a hierarchy of integro-differential equations relating $P^{(\lambda)}$ to all $P^{(\nu)}$, $\nu < \lambda$, can be easily derived by differentiating the defining equations of $P^{(\lambda)}$ with respect to the spatial variables. These equations, known as the BGKY (Born-Green-Kirkwood-Yvon) equations, can be generalized for present use in connection with systems exhibiting liquid-crystalline phases. Take $\rho(\varphi)$. It depends only on the angular variable φ . Differentiating Eq. (5) with respect to φ_1 and introducing the defining equations (6) and (8) of $g(r_{12}; \varphi_1, \varphi_2)$, one obtains the first BGKY equation:

$$-\frac{1}{\beta} \frac{\partial}{\partial \varphi_1} \ln \rho(\varphi_1) = \frac{n}{2\pi} \int_0^{2\pi} d\varphi_2 \\ \times \int_A d\vec{r}_2 \rho(\varphi_2) g(r_{12}; \varphi_1, \varphi_2) v_2(r_{12}) \\ \times \frac{\partial}{\partial \varphi_1} \cos 2\varphi_{12}. \quad (21)$$

In like manner one could differentiate Eq. (6) to obtain the second BGKY equation, one that relates $P^{(3)}$ to ρ and g . Somewhere along the line one truncates the hierarchy of equations by means of a closure approximation (such as a superposition approximation), and thereafter solves the remaining equations simultaneously for all low-order distribution functions including ρ and g . And since the

free energy of the system at every density n and temperature T can be expressed in terms of the distribution functions, one evaluates the free energy from which all thermodynamics flows. Actually for equations beyond Eq. (21), it is simpler to employ functional derivative techniques. There are more convenient equations than the BGKY equations which one can derive and use. The better known ones are the HNC (hypernetted chain) and the PY (Percus-Yevick). For liquid crystals, straightforward generalization of the definitions of functionals, functional derivatives, and functional inverses is sufficient. Compared to the usual procedure,²² the only modifications required are given below:

$$F\{f(\vec{r}, \varphi)\} = \int_0^{2\pi} d\varphi \int_A d\vec{r} f(\vec{r}, \varphi), \quad (22)$$

$$\frac{\delta}{\delta f(\vec{r}_2, \varphi_2)} F\{f(\vec{r}_1, \varphi_1)\} \\ = \lim_{\epsilon \rightarrow 0} \frac{1}{\epsilon} [F\{f(\vec{r}_1, \varphi_1) + 2\pi\epsilon \delta(\vec{r}_2 - \vec{r}_1) \delta(\varphi_2 - \varphi_1)\} \\ - F\{f(\vec{r}_1, \varphi_1)\}], \quad (23)$$

and

$$\int_0^{2\pi} d\varphi_2 \int_A d\vec{r}_2 h^{-1}(\vec{r}_1, \varphi_1; \vec{r}_2, \varphi_2) h(\vec{r}_2, \varphi_2; \vec{r}_3, \varphi_3) \\ = 2\pi \delta(\vec{r}_1 - \vec{r}_3) \delta(\varphi_1 - \varphi_3). \quad (24)$$

One then obtains the generalized Ornstein-Zernike equation²³:

$$g(r_{12}; \varphi_1, \varphi_2) - 1 = c(r_{12}; \varphi_1, \varphi_2) \\ + \frac{n}{2\pi} \int_0^{2\pi} d\varphi_3 \int_A d\vec{r}_3 [g(r_{13}; \varphi_1, \varphi_3) - 1] \\ \times c(r_{23}; \varphi_2, \varphi_3) \rho(\vec{r}_3, \varphi_3), \quad (25)$$

where $c(r_{12}; \varphi_1, \varphi_2)$ denotes the direct correlation function.²⁴ Approximate integral equations may then be derived by relating in various ways $g(r_{12}; \varphi_1, \varphi_2)$ and $c(r_{12}; \varphi_1, \varphi_2)$. In particular, the PY equation is obtained by making a functional Taylor-series expansion in the grand canonical

ensemble and retaining only up to the first derivative.²² Thus, one finds a second equation:

$$c(r_{12}; \varphi_1, \varphi_2) \approx g(r_{12}; \varphi_1, \varphi_2) \times (1 - e^{\beta[v_0(r_{12}) + v_2(r_{12}) \cos 2\varphi_{12}]}). \quad (26)$$

In this paper we employ the PY equation.

IV. REDUCTION OF THE INTEGRAL EQUATIONS

The substitution of expansion formulas (13) and (18) into Eqs. (21), (25), and (26) gives rise to an infinite set of coupled integral equations which are clearly unmanageable. The expansions must be truncated at an early stage. Moreover, the major effects of short-range correlations can be observed without the inclusion of complications like $G_m(r)$ and $G'_m(r)$. This amounts to choosing $g(r_{12}; \varphi_1, \varphi_2)$ to be $g(r_{12}; \varphi_{12})$, the isotropic pair correlation function; i.e., we shall assume the pair correlation to remain isotropic through the phase transition. In this case $\rho(r_3, \varphi_3)$ inside the integral in Eq. (25) can be taken to be a constant, namely unity. We therefore begin with

$$\rho(\varphi) \approx 1 + a_2 \cos 2\varphi + a_4 \cos 4\varphi \quad (27)$$

and

$$g(r_{12}; \varphi_1, \varphi_2) \approx g_I(r_{12}; \varphi_{12}) \approx G_0(r_{12}) + 2G_2(r_{12}) \cos 2\varphi_{12}. \quad (28)$$

Likewise for the direct correlation function we take

$$c(r_{12}; \varphi_1, \varphi_2) \approx c_I(r_{12}; \varphi_{12}) \approx C_0(r_{12}) + 2C_2(r_{12}) \cos 2\varphi_{12}. \quad (29)$$

The validity of such truncated expansions depends of course on the strength of the interaction and the density of the system. In subsequent work we intend to study the effects of higher-order terms and the range of validity. Our first task is to demonstrate that under such approximations the coupled integral equations possess solutions. Next we wish to compare these solutions with those of the mean-field theory.

Substituting Eqs. (28) and (29) into Eqs. (25) and (26), and decoupling, one finds

$$G_0(r_{12})e^{\beta v_0(r_{12})} g_0(\beta v_2(r_{12})) + 2G_2(r_{12})g_1(\beta v_2(r_{12}))e^{\beta v_0(r_{12})} = 1 + n \int_A d\vec{r}_3 \{G_0(r_{13}) - 1\} \{G_0(r_{23})[1 - e^{\beta v_0(r_{23})} g_0(\beta v_2(r_{23}))] - 2G_2(r_{23})e^{\beta v_0(r_{23})} g_1(\beta v_2(r_{23}))\} \quad (30)$$

and

$$G_2(r_{12})[g_0(\beta v_2(r_{12})) + g_2(\beta v_2(r_{12}))]e^{\beta v_0(r_{12})} + G_0(r_{12})g_1(\beta v_2(r_{12}))e^{\beta v_0(r_{12})} = n \int_A d\vec{r}_3 G_2(r_{13})[G_2(r_{23})\{1 - e^{\beta v_0(r_{23})}[g_0(\beta v_2(r_{23})) + g_2(\beta v_2(r_{23}))]\} - G_0(r_{23})e^{\beta v_0(r_{23})} g_1(\beta v_2(r_{23}))], \quad (31)$$

where g_m represents the modified Bessel function of m th order:

$$g_m(a) = \frac{1}{2\pi i} \oint e^{(a/2)(t+1/t)} \frac{dt}{t^{m+1}} \quad (a \text{ real}). \quad (32)$$

These equations can be cast in simpler forms:

$$\begin{aligned} \gamma_0(r)g_0(\beta v_2(r)) + 2\gamma_2(r)g_1(\beta v_2(r)) \\ = 1 + 2n \int_0^\infty s ds [\gamma_0(s)f_2(s) - 2\gamma_2(s)g_1(\beta v_2(s))] X(r, s) \end{aligned} \quad (33)$$

and

$$\begin{aligned} \gamma_0(r)g_1(\beta v_2(r)) + \gamma_2(r)[g_0(\beta v_2(r)) + g_2(\beta v_2(r))] \\ = 2n \int_0^\infty s ds [\gamma_2(s)f_3(s) - \gamma_0(s)g_1(\beta v_2(s))] Y(r, s), \end{aligned} \quad (34)$$

where

$$\gamma_0(r) = G_0(r)e^{\beta v_0(r)}, \quad (35)$$

$$\gamma_2(r) = G_2(r)e^{\beta v_0(r)}, \quad (36)$$

$$f_1(r) = e^{-\beta v_0(r)} - 1, \quad (37)$$

$$f_2(r) = e^{-\beta v_0(r)} - g_0(\beta v_2(r)), \quad (38)$$

$$f_3(r) = e^{-\beta v_0(r)} - g_0(\beta v_2(r)) - g_2(\beta v_2(r)), \quad (39)$$

$$X(r, s) = \int_0^\pi \{\gamma_0(|\vec{r} - \vec{s}|)[1 + f_1(|\vec{r} - \vec{s}|)] - 1\} d\theta, \quad (40)$$

$$Y(r, s) = \int_0^\pi \gamma_2(|\vec{r} - \vec{s}|)[1 + f_1(|\vec{r} - \vec{s}|)] d\theta, \quad (41)$$

and θ denotes the angle between \vec{r} and \vec{s} .

It is possible to solve the simultaneous equations (33) and (34) by various iterative procedures. In fact several were tried. The most efficient algorithm turned out to be the one in which $\gamma_0(r)$ and $\gamma_2(r)$ are simultaneously modified at every iteration. The numerical results reported in Sec. V were obtained with this method. Once $\gamma_0(r)$ and $\gamma_2(r)$, or

alternately $G_0(r)$ and $G_2(r)$, are found, the following moments of $v_2(r)$ can be evaluated:

$$\alpha_0 = -\beta n \int_A v_2(r) G_0(r) d\vec{r} \quad (42)$$

and

$$\alpha_2 = -\beta n \int_A v_2(r) G_2(r) d\vec{r}. \quad (43)$$

These are the crucial quantities in our theory because the substitution of Eqs. (27) and (28) into the first BGKY equation (21) results in the coupled transcendental equations:

$$\tau_2 = \frac{(1/2\pi) \int_0^{2\pi} \exp(\alpha_0 \tau_2 \cos 2\varphi + \frac{1}{2} \alpha_2 \tau_4 \cos 4\varphi) \cos 2\varphi d\varphi}{(1/2\pi) \int_0^{2\pi} \exp(\alpha_0 \tau_2 \cos 2\varphi + \frac{1}{2} \alpha_2 \tau_4 \cos 4\varphi) d\varphi} \quad (44)$$

and

$$\tau_4 = \frac{(1/2\pi) \int_0^{2\pi} \exp(\alpha_0 \tau_2 \cos 2\varphi + \frac{1}{2} \alpha_2 \tau_4 \cos 4\varphi) \cos 4\varphi d\varphi}{(1/2\pi) \int_0^{2\pi} \exp(\alpha_0 \tau_2 \cos 2\varphi + \frac{1}{2} \alpha_2 \tau_4 \cos 4\varphi) d\varphi} \quad (45)$$

which can be solved numerically or graphically with little effort.

V. NUMERICAL RESULTS

The numerical solution of Eqs. (33) and (34) for $\gamma_0(r)$ and $\gamma_2(r)$ was carried out on CDC 6400 and CDC 7600 computers. For the potential parameters, densities, and temperatures considered, we found the convergence of the iterative procedure to be sufficiently rapid to permit several sets of calculations. The energy parameters η and ϵ were measured in units of kT , so that keeping the ratio η/ϵ fixed a variation in η and ϵ corresponded to varying the temperature without altering the potential. We choose η and ϵ to be of the order of kT , and the range of the Gaussian, r_0 , to be arbitrarily twice the hard-core diameter σ . Since no experimental data are available at this moment, we have tried to keep the units of distance and density as flexible as possible. At a later stage one can adjust these by choosing a specific unit for distance and the corresponding inverse square for the unit of density. All integrations involving $G_0(r) - 1$ or $G_2(r)$ in the plane are carried out to a distance of approximately 7σ .

Figures 3 and 4 show the $G_0(r)$ and $G_2(r)$ obtained at two typical densities for

$$\epsilon = 1.50, \quad \sigma = 0.50, \quad \eta = 0.764, \quad r_0 = 1.00, \quad (46)$$

corresponding to temperature T_1 and $T_2 = 0.8988T_1$. In each figure the solid curves are at the lower density $n_1 = 0.75$. The dashed curves are at the higher density $n_2 = 0.95$. Note that $G_0(r)$ has the

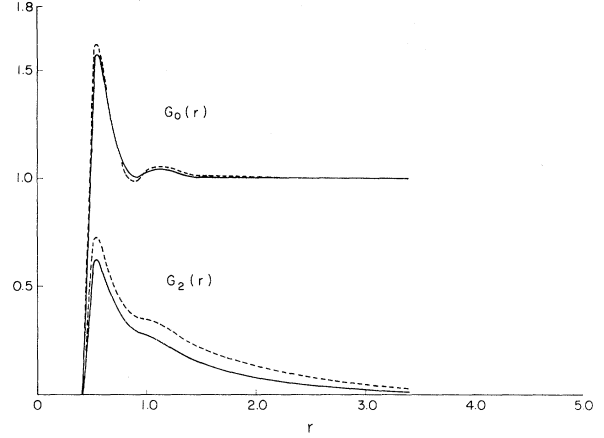


FIG. 3. $G_0(r)$ and $G_2(r)$ at temperature T_1 .

usual shape of a classical liquid, with sharpened features at higher density. It correctly approaches unity at large r . $G_2(r)$ decays toward zero with increasing r as expected. It is more pronounced at higher density, which indicates stronger orientational dependence of $g(r_{12}; \varphi_1, \varphi_2)$.

Figures 5 and 6 show the results of solving Eqs. (44) and (45). At this point one should recall that the order parameters τ_2 and τ_4 represent the one-particle distribution function or the density $\rho(\varphi)$. Below certain critical density $n_{NI}(T)$ Eqs. (44) and (45) only possess the trivial solutions $\tau_2 = 0, \tau_4 = 0$. The phase is clearly isotropic. Above $n_{NI}(T)$, a new set of nonvanishing solutions appear. So both isotropic and nematic phases become possible. To determine which is the stable phase, one must calculate and compare the free energies. To find a two-phase equilibrium region, one must carry out a Maxwell construction. Both topics lie outside the range of present interest. These will be dis-

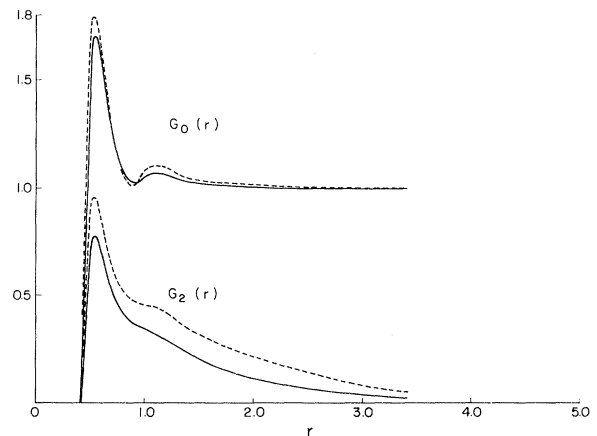


FIG. 4. $G_0(r)$ and $G_2(r)$ at temperature T_2 .

cussed in a forthcoming paper. In Figs. 5 and 6, the dashed curves represent mean-field results. We wish to conclude our discussion with (i) a brief review of the mean-field approximation as seen from the present theory, and (ii) a few remarks on how the present theory compares with mean-field calculations.

VI. COMPARISON WITH MEAN-FIELD THEORY

In the mean-field approximation the short-range correlations between molecules are discounted. What this means is that the two-particle distribution function $P^{(2)}(1, 2)$ can be decomposed into two one-particle distribution functions; thus

$$P^{(2)}(1, 2) \approx P^{(1)}(1)P^{(1)}(2). \quad (47)$$

By Eqs. (7) and (8), this implies

$$g(r_{12}; \varphi_1, \varphi_2) = 1, \quad (48)$$

or in the expansion formula (18) or (20),

$$G_0(r_{12}) = 1 \quad (49)$$

while all other coefficients $G_2(r_{12}) = \dots = 0$. Equation (21) for the density function $\rho(\varphi)$ reduces to

$$\begin{aligned} -\frac{1}{\beta} \frac{\partial}{\partial \varphi_1} \ln \rho(\varphi_1) \\ = \frac{n}{2\pi} \int_0^{2\pi} d\varphi_2 \int_A d\vec{r}_2 \rho(\varphi_2) v_2(r_{12}) \frac{\partial}{\partial \varphi_1} \cos 2\varphi_{12} \end{aligned} \quad (50)$$

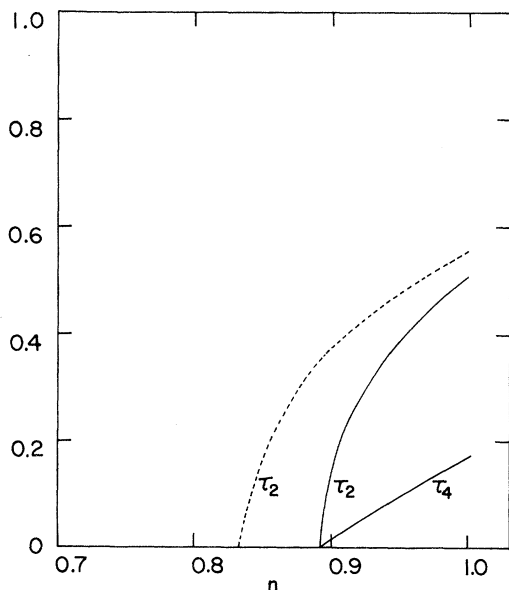


FIG. 5. Order parameters at temperature T_1 . The dashed curve represents the mean-field calculation.

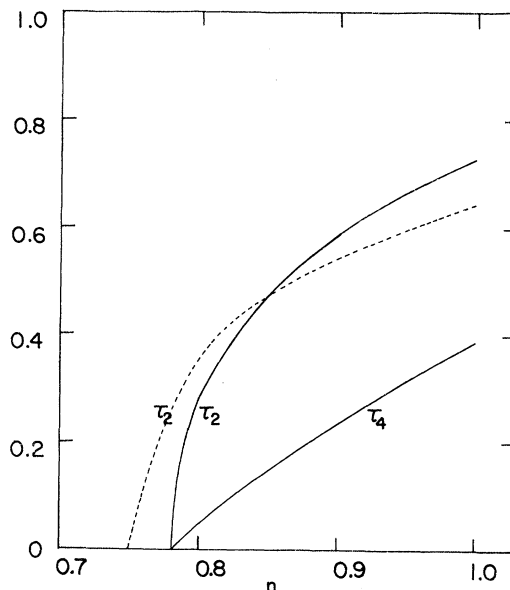


FIG. 6. Order parameters at temperature T_2 . The dashed curve represents the mean-field calculation.

or

$$\begin{aligned} \frac{\partial}{\partial \varphi_1} \ln \rho(\varphi_1) = \frac{\partial}{\partial \varphi_1} \left(\frac{-n}{2\pi kT} \right) \int_0^{2\pi} d\varphi_2 \\ \times \int_A d\vec{r} \rho(\varphi_2) v_2(r_{12}) \cos 2\varphi_{12}. \end{aligned} \quad (51)$$

This equation can be integrated readily to give

$$\rho(\varphi) = (1/\lambda) e^{-V(\varphi)/kT}, \quad (52)$$

with

$$V(\varphi_1) = \frac{n}{2\pi} \int_0^{2\pi} d\varphi_2 \int_A d\vec{r} \rho(\varphi_2) v_2(r) \cos 2\varphi_{12} \quad (53)$$

representing the mean field. λ in general should be a function of \vec{r}_1 . But in the present case we are concerned with the isotropic and nematic phases only. λ reduces to a normalization constant:

$$\lambda = (1/2\pi) \int_0^{2\pi} d\varphi e^{-V(\varphi)/kT}. \quad (54)$$

Note that the orientation-independent part $v_0(r)$ does not appear in our present consideration; i.e., it does not appear explicitly when one applies the mean-field approximation to isotropic and nematic phases. It has "averaged out" as in Ref. 1.

Solving Eq. (50) directly using the technique developed in this paper, we obtain

$$\tau_2 = \mathcal{G}_1(\pi r_0^2 n \eta \tau_2) / \mathcal{G}_0(\pi r_0^2 n \eta \tau_2). \quad (55)$$

Equation (55) can then be solved graphically. One

finds readily that nontrivial solutions exist as long as

$$\pi r_0^2 n \eta \geq 2.0. \quad (56)$$

In Ref. 2, the self-consistent equations (52) and (53) were solved approximately. In Ref. 3, a variational approach was employed in which the free-energy functional was numerically minimized with respect to a variational density function. The present approach, when generalized in a straightforward manner to allow for the smectic phase, is by far the simplest to use. Presently we are also in the process of calculating the effects of

short-range correlations in the smectic phase.

Results obtained for the potential parameters given in Eq. (46) are shown in Figs. 5 and 6 for two different temperatures. The major difference between the mean-field theory and our present theory is that τ_2 in the present theory drops more abruptly with decreasing density and rises to a higher plateau.

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