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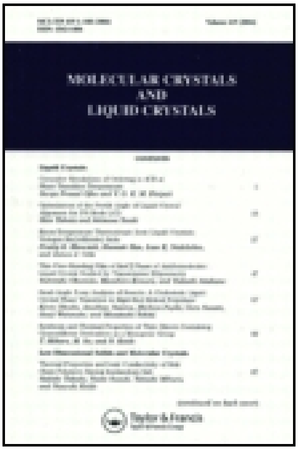

Molecular Crystals and Liquid Crystals

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Molecular Theories of Nematic Liquid Crystals

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Molecular Theories of Nematic Liquid Crystals

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In this paper, the current state of the art of molecular theories of nematic mesophases is reviewed. For this purpose, the many theories of nematogens which have been proposed are grouped into two classes: (1) the Maier-Saupe theory and its extensions and variants, which assume that nematic long-range order is primarily due to anisotropic intermolecular attractions and (2) the hard-rod and van der Waals theories, which assume that nematic order results primarily from excluded volume effects. These two types of theories are discussed in turn, with particular emphasis on the basic assumptions and approximations, the relative strengths and weaknesses, and the most fruitful applications of each of them. Finally, prospects for improving and extending current molecular theories are examined briefly.

I. INTRODUCTION

In this paper, I attempt to describe the current "state of the art" of molecular theories of rodlike nematogens. (The theory of disc-like nematogens is still in its infancy at this point.) In my assessment of various theoretical approaches, I have tried to be even-handed and "nonpartisan". Nonetheless, it should be emphasized that my conclusions represent the opinion of *one* theorist. Some of my colleagues may disagree with me on some points.

Since the pioneering work of Onsager,[1] Flory,[2] and Maier and Saupe,[3] a large number of molecular theories of nematics have been proposed. Quite conveniently for my purposes, all but a very few of these fall into one of the following two groups: (1) the Maier-Saupe theory and its extensions and variants and (2) the hard-rod and van der Waals theories. In the first group of theories, it is assumed that nematic long-range order results primarily from orientation-dependent intermolecular attractions, particularly London dispersion forces. Furthermore, explicitly or implicitly, it is assumed that short-range intermolecular repulsions can be treated as effectively spherically symmetric. (Since rodlike nematogens are clearly not spherical in shape, what is presumably being assumed is that the effects of the anisotropy in the short-range repulsions are very similar in nematic and isotropic phases and hence can be ignored.) In the second group of theories, on the other hand, nematic order is assumed to result primarily from the orientation-dependence of the very short-ranged intermolecular repulsions, which can be approximated by hard-core exclusions. In the hard-rod theories, there are no interactions between molecules other than the infinite repulsions which prevent overlaps; in the van der Waals theories, intermolecular attractions are superimposed on the hard-rod repulsions and the attractions are treated via some type of mean field approximation. An extensive (though certainly not complete) list of Maier-Saupe type theories,[3-15] hard-rod theories,[1,16-25] and van der Waals theories[2,26-40] is given in the bibliography of this paper. (To avoid inordinate length, this sampling includes only theories of pure thermotropic rodlike nematogens.)

It is clearly not possible, in a brief review paper, to discuss all these theories in turn or even to point out the differences between the various approaches within each group. Instead, I shall concentrate on one representative theory from each of the two groups: a generalization of the original Maier-Saupe theory[3] from the first group and a van der Waals theory developed by Gelbart and Baron[34] and by me[35] from the second group. The generalized Maier-Saupe theory and this van der Waals theory are discussed in Sections II and III, respectively. In each case, the basic assumptions, idealizations, and approximations of the theory are first discussed and then the numerical results obtained to date are summarized and compared with experimental data on common nematogens. Finally, in Section IV, the two groups of theories are compared with respect to their relative strengths and weaknesses, their most fruitful applications, and the prospects for improving and extending them.

II. THE GENERALIZED MAIER-SAUPE THEORY

The original mean field theory of Maier and Saupe[3] was first extended by Chandrasekhar and Madhusudana[4,41] and then cast in its most general form to date (for inflexible, cylindrically symmetric model molecules) by Humphries, James, and Luckhurst.[5] It is largely the latter generalization which is discussed below.[42]

A. Basic assumptions and approximations

In the derivation of their generalized Maier-Saupe theory, Humphries, James, and Luckhurst[5] (HJL) invoked the following idealizations and approximations.

1. Molecular flexibility was neglected; i.e., the potential energy of the system was assumed to depend only on the positions and orientations of the molecules, not on any conformational coordinates. Specifically, it was assumed that

$$U(\mathbf{r}^N, \Omega^N) = \sum_{i<j=2}^{N} v(\mathbf{r}_{ij}, \Omega_i, \Omega_j) = \sum_{i<j=2}^{N} [v_0(r_{ij}) + v_a(\mathbf{r}_{ij}, \Omega_i, \Omega_j)], \quad (1)$$

where $U(\mathbf{r}^N, \Omega^N)$ is the N-particle configurational energy, Ω_i and Ω_j represent the orientations of molecules i and j, and $\mathbf{r}_{ij}$ is the vector connecting their centers.

2. Cylindrical molecular symmetry was assumed. Ω thus represents a pair of angles: the polar angle θ and the azimuthal angle ϕ needed to specify the orientation of the symmetry axis of a molecule with respect to a space-fixed coordinate system with Z-axis parallel to the nematic director. In order to derive a general expression for the pair potential $v(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$, they began with the completely general expansion of Pople[43] for axially symmetric molecules; namely,

$$v(r, \theta_i', \phi_i', \theta_j', \phi_j') = 4\pi \sum_{L_1, L_2, m} u_{L_1L_2m}(r) Y_{L_1,m}(\theta_i', \phi_i') Y^*_{L_2,m}(\theta_j', \phi_j'), \quad (2)$$

where $r = |\mathbf{r}_{ij}|$, the $Y_{L,m}(\theta', \phi')$ are normalized spherical harmonics, and θ_i', ϕ_i', θ_j', and ϕ_j' are defined with respect to a coordinate system in which the intermolecular vector is the Z-axis. Transforming to the space-fixed coordinate system with Z-axis parallel to the nematic director, this becomes

$$v(r, \theta_i, \phi_i, \theta_j, \phi_j) = 4\pi \sum_{L, L_2, m} \sum_{p, q} u_{L_1L_2m}(r) Y_{L_1,p}(\theta_i, \phi_i) Y^*_{L_2,q}(\theta_j, \phi_j) D^{(L_1)}_{p,m} D^{(L_2)*}_{q,m} \quad (3)$$

where the $D^{(L_1)}_{p,m}$ and $D^{(L_2)}_{q,m}$ are the elements of Wigner rotation matrices.[44]

3. The mean field approximation was invoked to treat the orientation-dependent part of the intermolecular attractions (described by the pair potential $v_a(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$); i.e., the orientation-dependent attractions between a molecule with orientation Ω and all its neighbors were approximated collectively by the interaction of the given molecule with an average or mean field described by the pseudo-potential $\overline{\psi}_a(\Omega, \rho)$.

4. In evaluating $\overline{\psi}_a(\Omega, \rho)$, it was assumed that the neighbors of a molecule with orientation Ω are arranged about it in a spherically symmetric manner.

Given these assumptions and approximations, it can be shown that the mean field pseudo-potential $\overline{\psi}_a(\Omega, \rho)$, the orientational distribution function $f(\Omega)$, and the Helmholtz free energy A are given by

$$\overline{\psi}_a(\Omega, \rho) = -\sum_{n\geq 1} \varepsilon_{2n}(\rho)\eta_{2n}P_{2n}(\cos\theta) \tag{4}$$

$$f(\Omega) = \frac{\exp[-\beta\overline{\psi}_a(\Omega)]}{2\pi\int_0^\pi \exp[-\beta\overline{\psi}_a(\Omega)]\sin\theta d\theta}, \tag{5}$$

and

$$A = A_0 + NkT\int f(\Omega)\ln[4\pi f(\Omega)]d\Omega - \frac{1}{2}N\sum_{n\geq 1}\varepsilon_{2n}\eta_{2n}^2 \tag{6}$$

$$= A_0 + \frac{1}{2}N\sum_{n\geq 1}\varepsilon_{2n}\eta_{2n}^2 - NkT\ln\left\{\frac{1}{2}\int_0^\pi \exp[-\beta\overline{\psi}_a(\Omega)]\sin\theta d\theta\right\}, \tag{7}$$

where $\beta = 1/(kT)$, θ is the angle between the molecular symmetry axis and the nematic director, A_0 is the order-independent part of the free energy A, and η_{2n} and ε_{2n} are the average values of $P_{2n}(\cos\theta)$ and

$$\sum_{j=2}^{N}\sum_{m=-2n}^{2n} u_{2n2nm}(r_{ij}),$$

respectively. Finally, the order parameters η_{2n} are obtained by iterative solution of the consistency relations

$$\eta_{2n} = \int f(\Omega)P_{2n}(\cos\theta)\,d\Omega \tag{8}$$

$$= \frac{\int_0^\pi P_{2n}(\cos\theta)\exp[-\beta\overline{\psi}_a(\Omega)]\sin\theta\,d\theta}{\int_0^\pi \exp[-\beta\overline{\psi}_a(\Omega)]\sin\theta\,d\theta} \tag{9}$$

Approximation 4 above clearly is reasonable if and only if the very short-range repulsions between molecules are assumed to be at least approximately spherically symmetric. In this case, the short-range repulsions contribute to the isotropic part $v_0(r_{ij})$ of the intermolecular pair potential and the anisotropic part $v_a(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$ must be largely due to intermolecular attractions. Despite the generality of the pair potential (2), it is clear that the generalized Maier-Saupe theory is based on the underlying assumptions noted in the introduction; namely, (1) that nematic order results primarily from anisotropic intermolecular attractions and (2) that the very short-ranged repulsions between molecules can be assumed to be spherically symmetric. Finally, it is clear that the pseudo-potential (4) can be obtained starting from a much simpler expression for $v_a(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$; i.e.,

$$v_a(\mathbf{r}_{ij}, \Omega_i, \Omega_j) = \sum_{n \geq 1} u_{2n}(r_{ij}) P_{2n}(\cos \gamma_{ij}), \tag{10}$$

where γ_{ij} is the angle between the symmetry axes of molecules i and j.

B. Results

Numerical calculations have been carried out using two truncated versions of the pseudo-potential (4): in the original Maier-Saupe theory,[3]

$$\overline{\psi}_a = -\varepsilon_2(\rho)\eta_2 P_2(\cos \theta) \tag{11}$$

was used; Humphries, James, and Luckhurst[5] later used

$$\overline{\psi}_a = -\varepsilon_2(\rho)[\eta_2 P_2(\cos \theta) + \lambda \eta_4 P_4(\cos \theta)], \tag{12}$$

where $\lambda = \varepsilon_4(\rho)/\varepsilon_2(\rho) =$ a constant. Maier and Saupe assumed that $\varepsilon_2(\rho) \propto \rho^2$, while HJL obtained best agreement with experimental data by assuming that $\varepsilon_2 \propto \rho$.[4] It has been shown, however, that complete statistical mechanical self-consistency of the mean field theory requires $\varepsilon_n \propto \rho$ for all n.[45] This required density-dependence was used in all the calculations quoted below.

As is well known, the simple Maier-Saupe theory yields semi-quantitative agreement with experimental data on common nematogens. Moreover, this agreement can be improved substantially in several respects by the addition of the term proportional to $P_4(\cos \theta)$ to the mean field pseudo-potential. This can be seen clearly from Figures 1 and 2 and Table I.

In Figure 1, the order parameter η_2 is plotted versus reduced temperature $T^* = T/T_{NI}$ (T_{NI} is the nematic-isotropic transition temperature) for several nematogens at a constant pressure of one atmosphere, and these experimental data are compared with the predictions of the simple Maier-Saupe theory, given by curve A. [In calculating the theoretical curve A, it was assumed that $V^* = V/V_{NI} = \rho_{NI}/\rho$ is a universal function of T^* and experimental data were used to construct $V^*(T^*)$.][5] Although the Maier-Saupe prediction that η_2 should be a universal function of T^* is not borne

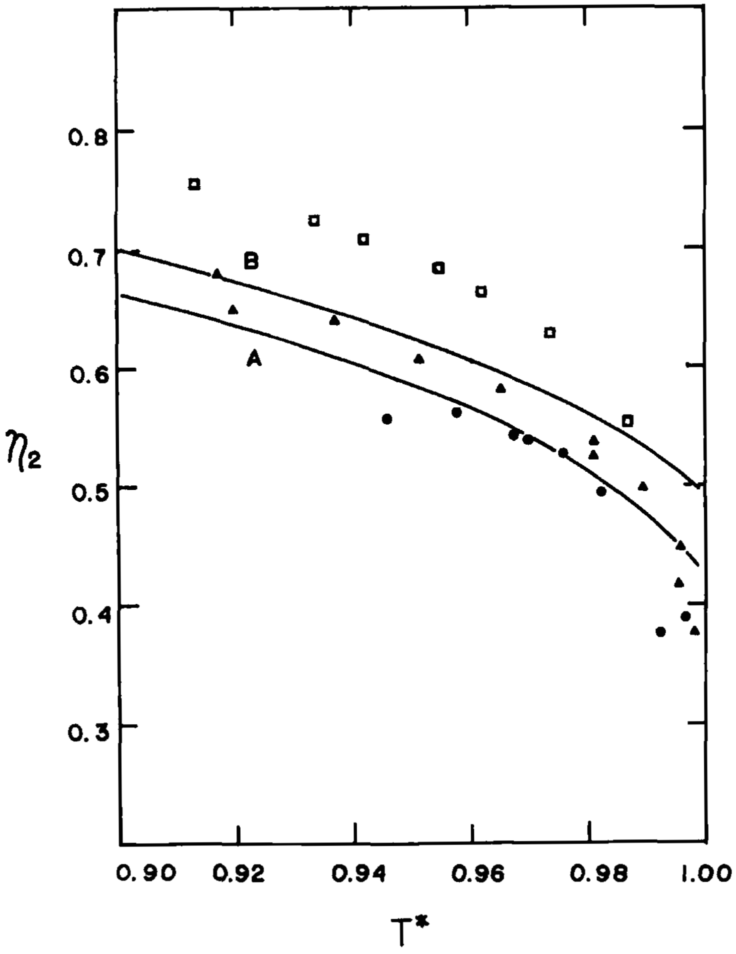

FIGURE 1 The temperature dependence of the order parameter η_2 at a constant pressure of 1 atm for *p*-azoxyanisole (●),[46] 2,4-nonadienoic acid (▲),[47] and *p*-azoxyphenetole (□).[46] Curve A is predicted by the simple Maier-Saupe theory with $\varepsilon_2 \propto \rho$. Curve B is predicted by the van der Waals theory with x = 1.75 and an empirical mean field pseudo-potential.

out by the experimental data, the theoretical curve $\eta_2(T^*)$ nonetheless has roughly the correct shape. If the HJL pseudo-potential is used instead, with suitable choices for the parameter λ, it is possible to fit the data on each of the three nematogens reasonably well.

The temperature-dependence of η_2 at constant density, rather than constant pressure, is shown in Figure 2. The experimental points are from the

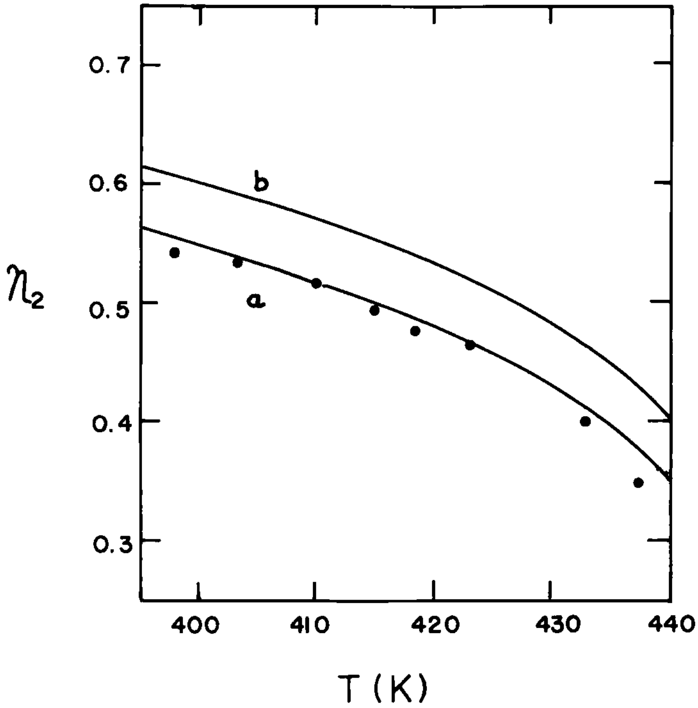

FIGURE 2 The temperature dependence of the order parameter η_2 at constant density: comparison between theory and experiment. The experimental points are from the data of McColl and Shih[48] for *p*-azoxyanisole. Curves b and a are the predictions of the simple Maier-Saupe theory and the HJL theory, respectively.

measurements of McColl and Shih[48] on *p*-azoxyanisole (PAA) at a constant molar volume of 221 cm^3; the curves marked b and a were obtained using the Maier-Saupe pseudo-potential and the HJL pseudo-potential with $\lambda = -0.187$, respectively. Finally, in Table I, experimental and theoretical values of the transition temperature, the entropy of transition, the order parameters η_2 and η_4, and the quantity $\tau = -\rho(\partial\eta_2/\partial\rho)_T/(T(\partial\eta_2/\partial T)\rho)$ at the *NI* transition for PAA are compared. The last quantity, first introduced by McColl and Shih,[48] is a measure of the relative sensitivity of the order parameter η_2 to changes in density versus changes in temperature. The generalized Maier-Saupe theory with $\varepsilon_n \propto \rho$, as is required for statistical mechanical self-consistency, predicts that $\tau = 1$ for all ρ and T. Aside from this difficulty and an overestimate of the entropy of transition, it is clear that using ε_2 and λ as adjustable parameters, the HJL approach yields rather good agreement with experiment.

TABLE I

Values of various quantities at the *NI* phase transition as predicted by the theories of Maier and Saupe (MS) and Humphries, James, and Luckhurst (HJL).

Quantity	Exp'tl data for PAA*	MS	Theoretical predictions HJL		
			$\lambda = -0.1$	$\lambda = -0.2$	$\lambda = -0.3$
T_{NI}	409K	409K	409K	409K	409K
η_2	0.36	0.429	0.398	0.372	0.353
η_4	0.07	0.120	0.098	0.081	0.070
$\Delta S/(Nk)$	0.17	0.417	0.358	0.314	0.282
τ	4.0	1	1	1	1

*For the references from which these values were taken, see Ref. 39b.

III. THE VAN DER WAALS THEORY

A. Basic assumptions and approximations

The van der Waals theories of nematic liquids, like the van der Waals theory of simple liquids,[49] are based on the assumption that the structure of a liquid far from its gas-liquid critical point is largely determined by very short-ranged intermolecular repulsions, which can be approximated satisfactorily by hard-core exclusions. In deriving the present version of the theory,[34,35] the following idealizations and approximations are invoked:

1. Molecular flexibility is again neglected and a nematogen is modeled as an inflexible object with some average or effective shape. In this instance, it is assumed that

$$\begin{aligned} U(\mathbf{r}^N, \Omega^N) &= \sum_{i<j=2}^{N} v(\mathbf{r}_{ij}, \Omega_i, \Omega_j) \\ &= \sum_{i<j=2}^{N} [v_{rep}(\mathbf{r}_{ij}, \Omega_i, \Omega_j) + v_{att}(\mathbf{r}_{ij}, \Omega_i, \Omega_j)] \end{aligned} \tag{13}$$

where v_{rep} is a very short-ranged repulsive potential and v_{att} is a somewhat longer-ranged attractive potential.

2. The very short-range intermolecular repulsions are approximated by hard-rod exclusions; i.e., it is assumed that

$$v_{rep}(\mathbf{r}_{ij}, \Omega_i, \Omega_j) = v^*(\mathbf{r}_{ij}, \Omega_i, \Omega_j) = \begin{cases} \infty \text{ if the hard cores of } i \\ \quad \text{and } j \text{ would overlap} \\ 0 \text{ otherwise} \end{cases} \tag{14}$$

3. The rodlike molecular hard cores are assumed to have cylindrical symmetry. Ω thus again represents the pair of Euler angles (θ, ϕ).

4. Intermolecular attractions are treated via the mean field approximation; i.e., the attractions between a molecule with orientation Ω and all its neighbors are approximated collectively by the interaction of the given molecule with a spatially uniform mean field $\overline{\psi}(\Omega, \rho)$. Two different approaches have been used to evaluate the pseudo-potential $\overline{\psi}(\Omega, \rho)$.

(a) In the empirical approach first used in Ref. 35a, the pseudo-potential was assumed to have the simple form

$$\overline{\psi}(\Omega, \rho) = -v_0\rho - v_2\rho\eta_2 P_2(\cos\theta) \tag{15}$$

where v_0 and v_2 are positive constants, θ is the angle between the molecular long axis and the nematic director, and P_2 and η_2 are again the second order Legendre polynominal and the nematic order parameter, respectively. In this approach, v_0 and v_2 are treated as adjustable parameters and no attempt is made to calculate them from an assumed attractive potential $v_{att}(\mathbf{r}_{ij}, \Omega_i, \Omega_j)$.

(b) In the generalized van der Waals theory of Gelbart and Baron,[34] on the other hand, $\overline{\psi}$ is related to the intermolecular potential of attraction v_{att} by the equation

$$\overline{\psi}(\Omega, \rho) = \rho\int d\Omega' f(\Omega') \int e^{-\beta v^*(\mathbf{r},\Omega,\Omega')} v_{att}(\mathbf{r}, \Omega, \Omega')\, dr, \tag{16}$$

where $\mathbf{r}$ is the vector connecting the centers of two molecules with orientations Ω and Ω', respectively.

Having made these assumptions and approximations, it can be shown that the Helmholtz free energy functional for the model system is given by

$$A[f(\Omega)] = A^*[f(\Omega)] + \frac{1}{2}N\int f(\Omega)\overline{\psi}(\Omega)\, d\Omega, \tag{17}$$

where $A^*[f(\Omega)]$ is the free energy functional for a system of hard rods constrained to have orientational distribution function $f(\Omega)$. The most convenient shape for the molecular hard cores is a spherocylinder (i.e., a right circular cylinder capped on each end by a hemisphere of the same radius), because the mutual exclusion volume of two spherocylinders has a particularly simple dependence on their relative orientations. Since the Helmholtz free energy of a fluid of hard spherocylinders cannot be derived exactly and has not been calculated numerically, one must resort to some approximate statistical mechanical method to evaluate $A^*[f(\Omega)]$. In the numerical calculations done to date, the approach used has almost always been scaled particle theory (SPT). (See Ref. 24c for a discussion of the SPT of hard spherocylinders.) After $A^*[f(\Omega)]$ obtained in this manner has been substituted in (17), minimization of the functional $A[f(\Omega)]$ yields the following nonlinear integral equation for $f(\Omega)$:

$$f(\Omega) = C \exp\left\{-\left[\beta\bar{\psi}(\rho,\Omega) + \lambda(x,v_0\rho)\int d\Omega' f(\Omega')|\sin\,\gamma(\Omega,\Omega')|\right]\right\}, \tag{18}$$

where C is a normalization constant, x and v_0 are the length-to-width ratio and the volume, respectively, of a molecular hard core, and γ is the angle between the long axes of two molecules with orientations Ω and Ω', respectively. (For a spherocylinder with radius a and cylindrical length l, $x = l/2a + 1$ and $v_0 = \pi a^2 l + (4/3)\pi a^3$.) The precise form of the function $\lambda(x, v_0\rho)$ depends on which of the several slightly different versions of scaled particle theory[19,20,23,24] one uses to derive $A^*[f(\Omega)]$; in the version[24b,c] used most often in calculations, for example,

$$\lambda(x, v_0\rho) = \frac{24(x-1)^2 v_0\rho[1-(x-1)v_0\rho/(3x-1)]}{\pi(3x-1)(1-v_0\rho)^2}. \tag{19}$$

B. Results

Calculations using the empirical pseudo-potential (15) have been carried out by me[35a] (for molecules with $x = 3$) and by Savithramma and Madhusudana[39] (for molecules with various values of x between 1 and 2.45). For model systems with $x = 3$ (a seemingly reasonable a priori estimate of the effective length-to-width ratio of a number of nematogens), only qualitative agreement with experiment is obtained; in particular, the predicted values of the order parameters η_2 and η_4 are too large and the strength of the first-order NI transition is substantially exaggerated. On the other hand, if one uses length-to-width ratios somewhat smaller than might be predicted a priori and treats the coefficients υ_0 and υ_2 as adjustable parameters, this approach yields rather good semi-quantitative agreement with experiment. This can be seen from curve B in Figure 1 and from the first two columns in Table II, which compare experimental data for PAA with $\eta_2(T)$ at constant P and the properties of the NI transition, respectively, for a model system with $x = 1.75$.[39b] (In comparing the predictions of the van der Waals approach with those of the Maier-Saupe and HJL approaches, it should be kept in mind that much more is being asked of the former than of the latter; i.e., in the latter approaches, one calculates only the difference in free energy between a nematic and an isotropic phase at a given T and ρ and obtains $\rho(T,P)$ from experiment when needed; in the former approach, one calculates the equation of state and the free energy of the isotropic phase as well.)

TABLE II

Values of various quantities at the *NI* phase transition as predicted by the van der Waals theory with an empirical mean field potential and by the generalized van der Waals (GVDW) theory. $P = 1$ atm in all cases.

Quantity	Exp'tl data for PAA	Theoretical predictions $x = 1.75$	$x = 2$	$x = 2$
		Empirical $\overline{\psi}(\Omega,\rho)$	GVDW theory	GVDW theory "Corrected"
T_{NI}	409K	409K	408.4K	408.8K
$v_0\rho_{nem}$	0.62	0.62	0.456	0.556
$\Delta\rho/\rho_{nem}$	0.0035	0.0070	0.116	0.012
η_2	0.36	0.499	0.816	0.476
η_4	0.07	0.173	0.572	0.149
$\Delta S/(Nk)$	0.17	0.62	2.65	0.599
τ	4.0	3.9	1.65	3.53
$(dT_{NI}/dP)_{P=1\ \mathrm{atm}}$	48K/kbar	31K/kbar	184K/kbar	61K/kbar

Calculations of thermodynamic properties of nematogens using the generalized van der Waals theory, in which $\overline{\psi}(\Omega, \rho)$ is given by (16) have been carried out by Baron and Gelbart[50] and by me.[51] In the former instance, the orientational distribution function $f(\Omega)$ was approximated by the one-parameter variational form

$$f(\Omega) = \frac{\cosh(\alpha\cos\theta)}{\displaystyle\int_0^{\pi} \cosh(\alpha\cos\theta)\,\sin\theta\, d\theta} \tag{20}$$

first suggested by Onsager.[1] (α is evaluated by minimization of the Helmholtz free energy.) In the second instance, $f(\Omega)$ was obtained from the integral equation (18), which was solved numerically by expanding $\ln f(\Omega)$ in even-order Legendre polynominals through P_{20} (cos θ). Since (20) can be shown[51] to be rather poor approximation to the solution of equation (18), the later set of calculations clearly provide the more accurate test of the generalized van der Waals theory.

From the results reported in Ref. 51, it is clear that when $\overline{\psi}(\Omega, \rho)$ is calculated using the generalized van der Waals prescription (16), the agreement between theory and experiment is considerably poorer than when an empirical pseudo-potential with two adjustable parameters is used. This can be seen by comparing columns 1, 2, and 3 in Table II, where column 3 gives results obtained using (16) and a model system with hard-core length-to-width ratio x = 2 and an attractive potential $v_{att} = -\varepsilon_0/r^6$ between molecules, where ε_0 was chosen to produce $T_{NI} \approx$ 409K. From this comparison, it is also clear that the generalized van der Waals theory, in its present form, greatly exaggerates the degree of orientational order in the nematic phase and the strength of the first-order *NI* transition even when an *isotropic* attractive potential v_{att} is used. In Ref. 51, it was argued that the most important cause of the quantitative deficiencies of the theory is probably the neglect of short-range orientational order in the evaluation of $\bar{\psi}(\Omega, \rho)$ using (16). In order to obtain a rough estimate of the order of magnitude of the errors caused by this neglect of short-range order, the calculations were redone for two model systems with $x = 2$ and $x = 3$, respectively, using a very crude and highly arbitrary procedure for mimicking the effects of short-range orientational correlations when evaluating $\bar{\psi}(\Omega, \rho)$. The precise procedure used was as follows: when integrating $v_{att}(\mathbf{r}, \Omega, \Omega')$ over $\mathbf{r}$ and Ω' to obtain $\bar{\psi}(\Omega, \rho)$, a spherocylindrical volume of radius $2a(1 + \alpha)$ and cylindrical length l surrounding the molecule with orientation Ω was defined, and it was assumed that all molecules whose centers lie within this volume also have orientation Ω. (a and l are the radius and cylindrical length, respectively, of a spherocylindrical hard core.) Outside this spherocylindrical volume, the density of molecules with orientation Ω' was again assumed to be $e^{-\beta v^*}\rho f(\Omega')$. For both systems considered, α was set equal to $l/(8a)$, which means that the radius $2a(1 + \alpha)$ is midway between the respective distances of closest approach of two parallel and two perpendicular molecular hard cores.

The results of these revised calculations for the model system with $x = 2$ are given in column 4 of Table II, from which it is clear that the incorporation of short-range orientational order—however crudely and arbitrarily it was done—leads to dramatically improved agreement with experiment. This argues quite strongly that the neglect of short-range orientational order is indeed a very serious source of error and that in attempting to improve the generalized van der Waals theory, top priority should be given to trying to incorporate short-range orientational correlations into the theory in some approximate but self-consistent manner.

IV. COMPARISONS AND CONCLUSIONS

Having described a representative Maier-Saupe and van der Waals theory of nematics, I should now like to discuss the relative strengths and weaknesses and the most fruitful applications of each of these types of approaches. (Hard-rod theories of nematics will not be included in these comparisons because I view them simply as precursors of the van der Waals theories.) Finally, suggested improvements and extensions of each type of theory will be described briefly.

A. Relative strengths and weaknesses

The great strength of the Maier-Saupe-type theories is their impressive combination of simplicity and success. If one were to rank theories of nematics on the basis of the quality of their numerical predictions divided by the amount of computational effort required, the Maier-Saupe theory with the simple pseudo-potential (11) would certainly be in first place. Because of its great simplicity, it is relatively easy to extend the theory to treat mesogenic systems other than rigid, cylindrically symmetric model nematogens. As a result, Maier-Saupe-like approaches have been used to study nematogens with semiflexible molecular "tails",[8] nematogens without cylindrical symmetry,[9] mixtures of nematogens,[52] cholesterics,[53] smectics,[54,55] disc-like mesogens,[56,57] and mesogens exhibiting "reentrant" mesophases,[58] among others. Furthermore, as a result of the great simplicity of the Maier-Saupe approach, it is possible to go beyond the mean field approximation; i.e., it is possible to treat a model system with the simple pair potential

$$v(r_{ij},\gamma_{ij}) = u_0(r_{ij}) + u_a(r_{ij})P_2(\cos\gamma_{ij}) \qquad (21)$$

without invoking the mean field approximation. The properties of the *NI* phase transition have, in fact, been calculated for such a model system (or its nearest-neighbor lattice analog) using constant coupling theory,[10] the random phase approximation,[11c] various versions of the Bethe approximation,[6,11a,b] and computer simulation.[59]

On the other hand, Maier-Saupe-type theories of nematogens have two relative weaknesses, in my opinion. First, their basic assumptions are not very reasonable physically. Assuming that the distribution of its neighbors about a given molecule is spherically symmetric is clearly quite unrealistic for typical rodlike nematogens. Moreover, assuming that one can ignore the role of "packing effects" in producing nematic long-range order flies in the face of what has been learned from the theory of simple liquids; namely, that the structure of such a liquid far from the gas-liquid critical point is essentially determined by very short-ranged repulsions between molecules.[60] Secondly, it is very difficult to relate the parameters of Maier-Saupe-type theories to the molecular properties of individual nematogens. (For example, one has no idea how to relate the parameter λ appearing in the HJL pseudo-potential to molecular size, shape, polarity, polarizability, etc.) As a result, this class of theories is not very useful for chemical purposes; i.e., for investigating the precise relationship between molecular structure and mesomorphic behavior.

In my opinion, the van der Waals theories of nematics have two relative strengths. First, their basic assumptions seem more physically reasonable than those of the Maier-Saupe-type theories — in the light of what has been learned about the prime importance of short-range intermolecular repulsions in ordinary isotropic liquids (see above). Secondly, van der Waals theories are clearly more useful for chemical purposes. In particular, the ability to vary independently the size and shape of the model molecules, on one hand, and the strength, anisotropy, and separation-dependence of the intermolecular attractions, on the other hand, makes it *relatively* straightforward to relate the parameters of the given theory to the structure, flexibility, polarity, polarizability, etc., of individual mesogens.

On the other hand, the major relative weakness of the van der Waals theories is their computational complexity relative to Maier-Saupe-type theories. Although van der Waals theories using lattice models or continuum models with a small set of allowed orientations have been employed to treat nematogens with semiflexible "tails,"[22,37] nematogens without cylindrical hard-core symmetry,[61,62] and nematogens which also exhibit smectic/crystalline phases,[32,33,63] such extensions are relatively quite difficult using a translational and orientational continuum model, because of the necessity of specifying the precise shape of the molecular hard cores and of evaluating the orientation-dependent hard-core mutual exclusion volume. In this respect, extensions are most difficult if one uses the generalized van der Waals approach, in which one must evaluate the mean field potential $\overline{\psi}(\Omega, \rho)$ by averaging the intermolecular potential of attraction v_{att} $(\mathbf{r}, \Omega, \Omega')$ over all allowed relative positions and orientations of a pair of molecules.

B. Most fruitful applications

The most fruitful application of the Maier-Saupe theory and its descendants would seem to be the study of phase transitions and associated critical phenomena in mesogenic systems. For such investigations, it is important that the statistical mechanics be done as accurately as possible, but the molecular details of the model system are presumably not important as long as the model Hamiltonian has the correct symmetry. This suggests that one use the simplest possible Hamiltonian which has the correct symmetry properties and will produce the phase of interest. For example, the simple Maier-Saupe model with pair potential (11) or its nearest-neighbor lattice analog would seem to be the appropriate choice for studying the *NI* transition, while McMillan's extension of the Maier-Saupe model[54a] would seem best suited for studying the nematic-smectic A transition. Finally, a closely related fruitful application of Maier-Saupe-type theories is the study of the relationship between the symmetry of the intermolecular pair potential and the occurrence and properties of various mesophases. In this spirit, extensions of the Maier-Saupe theory have been applied to cholesterics,[53] smectic C mesophases,[54b] and ordered smectic mesophases.[55]

On the other hand, the most fruitful application of the van der Waals theories of nematics is clearly the study of the relationship between molecular structure and mesophase stabilities and properties. As has been noted, in order for a molecular theory to be used successfully to study this extremely important relationship, it is necessary that the parameters of the theory can be related to the molecular size, shape, flexibility, polarity, polarizability, etc., of a particular mesogen in some reasonably straightforward manner. Furthermore, although quantitative agreement between theory and experiment is certainly not required, the agreement must be good enough so that one can believe qualitative trends and explanations suggested by the theory, even rather subtle ones. The latter requirement suggests that one use, whenever possible, a model system in which the molecules are permitted to adopt a continuous range of positions and orientations, rather than a more highly idealized lattice model or model with a small set of allowed orientations. Among van der Waals theories using such a continuum model, it is clear that the generalized van der Waals theory, despite its greater complexity and present quantitative deficiencies, is better suited for chemical purposes than the simpler approaches[35a,36,39] employing an empirical mean field potential $\overline{\psi}(\Omega, \rho)$, since, in the latter, there is no straightforward way to relate the strength of the anisotropic term in $\overline{\psi}$ to the characteristics of a particular nematogen.

C. Suggested improvements and extensions

In my opinion, the most desirable improvement which could be made to the generalized Maier-Saupe theory would be to abandon the assumption that the "effective" intermolecular pair potential between two molecules i and j depends only on $r_{ij} = |\mathbf{r}_{ij}|$ and $\hat{\Omega}_i \cdot \hat{\Omega}_j$ where $\hat{\Omega}_i$ and $\hat{\Omega}_j$ are unit vectors parallel to the symmetry axes of the two molecules. Leaving aside all arguments concerning the relative importance of intermolecular attractions and repulsions, one can argue, on symmetry grounds alone, that for axially symmetric particles with end-to-end symmetry as well, the pair potential should also depend on $\hat{r}_{ij} \cdot \hat{\Omega}_i$ and $\hat{r}_{ij} \cdot \hat{\Omega}_j$, where $\hat{r}_{ij} = \mathbf{r}_{ij}/|\mathbf{r}_{ij}|$. If one views the Maier-Saupe theory merely as the simplest possible approach which yields a stable nematic phase with reasonable properties, then adding the dependence on the latter two variables would be an unwarranted complication. On the other hand, if one views the theory as providing the framework for a quite general theory of nematogens, then starting with a pair potential which depends on r_{ij}, $\hat{\Omega}_i \cdot \hat{\Omega}_j$, $\hat{r}_{ij} \cdot \hat{\Omega}_i$, and $\hat{r}_{ij} \cdot \hat{\Omega}_j$ in some reasonable manner, would be a big step forward. This point of view has been espoused by Shen *et al.*,[64] who advocated using a pair potential of the form

$$v(i,j) = v_0(r_{ij}) + v_2(r_{ij})P_2(\hat{\Omega}_i \cdot \hat{\Omega}_j) + w_2(r_{ij})[P_2(\hat{\Omega}_i \cdot \hat{r}_{ij}) + P_2(\hat{\Omega}_j \cdot \hat{r}_{ij})] \tag{22}$$

More recently, Ruijgrok and Sokalski[65] have presented a simple theory of nematics based on a Corner potential[66] which depends on $\hat{\Omega}_i \cdot \hat{r}_{ij}$ and $\hat{\Omega}_j \cdot \hat{r}_{ij}$ as well as r_{ij} and $\hat{\Omega}_i \cdot \hat{\Omega}_j$.

As noted previously, the Maier-Saupe theory has already been extended to treat a large number of mesogenic systems besides simple model nematogens. Among these extensions, it seems to me that further work could most profitably be done on models for disc-like mesogens and ordered smectic phases. It also appears that some points of contention still need to be resolved concerning the extension of the Maier-Saupe approach to cholesterics.[53]

Let us now turn to improvements and extensions of the van der Waals theories of nematics. The discussion of suggested improvements will focus on the generalized van der Waals theory, since it is the most ambitious van der Waals approach and seems best suited, at least in principle, for the chemical task of studying the relationship between molecular structure and mesomorphism. The discussion of suggested extensions will be more general in scope.

As has been noted, the most promising way to improve the generalized van der Waals theory would seem to be to take short-range orientational order into account in some approximate but self-consistent manner. Possible ways to accomplish this include using some modification of the Bethe approximation, using clusters of highly oriented molecules as the basic unit in the calculations, and replacing the weighting function $\rho f(\Omega')e^{-\beta v^*}$ in (16) by $\rho f(\Omega')e^{-\beta v^*}y(\mathbf{r}, \gamma)$, where $e^{-\beta v^*}y$ represents some density-independent approximation to the hard-rod pair correlation function.[51] Secondly, it appears that the use of molecular hard cores without cylindrical symmetry would also lead to significantly improved agreement with experiment, since calculations by a number of authors,[7,9,61,62] using a variety of approximate theoretical techniques, suggest that the assumption of cylindrical molecular symmetry leads to substantial overestimates of the degree of order in the nematic phase and of the discontinuities in ρ, H, S, η_2, η_4, etc., at the *NI* transition. (A promising hard-core shape to try to use would be a "capped parallelepiped" or "stretched spherocylinder;" i.e., a parallelepiped with edges of length a, b, and l capped on the surfaces of area $a \times l$ and area $a \times b$ by half spherocylinders of radius a and cylindrical lengths l and b, respectively.) Finally, the theory might also be improved by evaluating the hard-core free energy functional $A^*[f(\Omega)]$ using a more accurate technique than scaled particle theory. Possible approaches of this sort have been suggested by Savithramma and Madhusudana[39a] and Barboy and Gelbart.[67]

Various van der Waals theories of rigid nematogens have been extended to treat more complicated mesogenic systems. In addition to the extensions already mentioned (section IV A above), van der Waals theories with lattice models have been used to treat nematogenic solutions,[68] while "continuum" van der Waals theories have been used to treat nematogenic solutions,[69] nematic mesophases subject to elastic deformations,[70] and disc-like nematogens.[71] Future extensions that would be particularly desirable, in my opinion, include (1) extending the generalized van der Waals theory to allow for the occurrence of smectic as well as nematic ordering; (2) modifying the generalized van der Waals theory to take into account the semiflexibility of the molecular "tails" of many real mesogens; (3) developing a van der Waals lattice model for nematogens/smectogens which simultaneously takes "tail" semiflexibility into account and can treat smectic, nematic, and isotropic phases and (4) using both the generalized van der Waals approach and van der Waals theories with lattice models to study the relative stabilities of smectic A and C and the more ordered smectic mesophases. A student of mine is presently working on the third of these suggested extensions.

References

1. L. Onsager, *Ann. N.Y. Acad. Sci.*, **51**, 627 (1949).
2. P. J. Flory, *Proc. Roy. Soc.*, (London) **A234**, 73 (1956).
3. W. Maier and A. Saupe, *Z. Naturforsch.*, **14a**, 882 (1959); **15a**, 287 (1960).
4. S. Chandrasekhar and N. V. Madhusudana, *Acta Cryst.*, **A27**, 303 (1971).
5. R. L. Humphries, P. G. James and G. R. Luckhurst, *J. Chem. Soc. Faraday Trans. II*, **68**, 1031 (1972).
6. N. V. Madhusudana and S. Chandrasekhar, *Solid State Comm.*, **13**, 377 (1973); N. V. Madhusudana, K. L. Savithramma and S. Chandrasekhar, *Pramana*, **8**, 22 (1977).
7. J. P. Straley, *Phys. Rev. A*, **10**, 1881 (1974).
8. S. Marčelja, *J. Chem. Phys.*, **60**, 3599 (1974).
9. G. R. Luckhurst, C. Zannoni, P. L. Nordio and U. Segre, *Mol. Phys.*, **30**, 1345 (1975).
10. P. Sheng and P. J. Wojtowicz, *Phys. Rev. A*, **14**, 1883 (1976).
11. (a) J. G. J. Ypma and G. Vertogen, *J. de Phys.*, **37**, 557 (1976); (b) J. G. J. Ypma, G. Vertogen and H. T. Koster, *Mol. Cryst. Liq. Cryst.*, **37**, 57 (1976); (c) G. Vertogen and B. W. van der Meer, *Phys. Rev. A*, **19**, 370 (1979).
12. J. G. J. Ypma and G. Vertogen, *Phys. Lett.*, **60A**, 212 (1977).
13. M. A. Lee and C-W Woo, *Phys. Rev. A*, **16**, 750 (1977).
14. V. T. Rajan and C-W Woo, *Phys. Rev. A*, **17**, 382 (1978).
15. L. Longa, *Acta Phys. Pol.*, **A60**, 513 (1981).
16. A. Isihara, *J. Chem. Phys.*, **19**, 397 (1951).
17. E. A. DiMarzio, *J. Chem. Phys.*, **35**, 658 (1961).
18. R. Zwanzig, *J. Chem. Phys.*, **39**, 1714 (1963).

19. M. A. Cotter and D. E. Martire, *J. Chem. Phys.*, **53**, 4500 (1970).
20. G. Lasher, *J. Chem. Phys.*, **53**, 4141 (1970).
21. L. K. Runnels and C. Colvin, *J. Chem. Phys.*, **53**, 4219 (1970).
22. G. Ågren and D. E. Martire, *J. Chem. Phys.*, **61**, 3959 (1974).
23. K. M. Timling, *J. Chem. Phys.*, **61**, 465 (1974).
24. M. A. Cotter, (a) *Phys. Rev. A*, **10**, 625 (1974); (b) *J. Chem. Phys.*, **66**, 1098 (1977), Appendix; (c) in "The Molecular Physics of Liquid Crystals", G. R. Luckhurst and G. W. Gray, editors (Academic Press, London, 1979), Chapter 7.
25. S. D. P. Flapper and G. Vertogen, *J. Chem. Phys.*, **75**, 3599 (1981).
26. M. A. Cotter and D. E. Martire, *Mol. Cryst. Liq. Cryst.*, **7**, 295 (1969).
27. R. Alben, *Mol. Cryst. Liq. Cryst.*, **13**, 193 (1971).
28. A. Wolf and A. G. DeRocco, *J. Chem. Phys.*, **55**, 12 (1971).
29. P. Papon and J. P. LePesant, *Chem. Phys. Lett.*, **12**, 331 (1971).
30. P. Sheng, *J. Chem. Phys.*, **59**, 1942 (1973).
31. H. Kimura, *J. Phys. Soc. Japan*, **36**, 1280 (1974).
32. K. Miyakawa, N. Hijikuro and H. Mori, *J. Phys. Soc. Japan*, **36**, 944 (1974); N. Hijikuro, K. Miyakawa and H. Mori, *J. Phys. Soc. Japan*, **37**, 928 (1974).
33. M. A. Cotter, *Mol. Cryst. Liq. Cryst.*, **35**, 33 (1976).
34. W. M. Gelbart and B. A. Baron, *J. Chem. Phys.*, **66**, 207 (1977).
35. M. A. Cotter, *J. Chem. Phys.*, *(a)*, **66**, 1098 (1977); (b) **66**, 4710 (1977).
36. J. G. J. Ypma and G. Vertogen, *Phys. Rev. A*, **17**, 1490 (1978).
37. F. Dowell and D. E. Martire, *J. Chem. Phys.*, **68**, 1088; 1094 (1978).
38. P. J. Flory and G. Ronca, *Mol. Cryst. Liq. Cryst.*, **54**, 289 (1979).
39. K. L. Savithramma and N. V. Madhusudana, (a) *Mol. Cryst. Liq. Cryst.*, **62**, 63 (1980); (b) *Mol. Cryst. Liq. Cryst.*, in press.
40. M. Warner, *Mol. Cryst. Liq. Cryst.*, **80**, 79 (1982).
41. Strictly speaking, the theory of Chandrasekhar and Madhusudana should not be placed in the Maier-Saupe group of theories, since it does not treat intermolecular repulsions as spherically symmetric. (Instead, a molecule is assumed to possess three centers of repulsion, near the center and each end, respectively, which interact with centers of repulsion on other molecules via a repulsive potential varying as r^{-12}.) Nonetheless, I have included this approach among the extensions of the Maier-Saupe theory because it was clearly intended as such and because it produces results quite similar to those of the HJL theory.
42. For a more recent review of the HJL approach, see G. R. Luckhurst, in "The Molecular Physics of Liquid Crystals", G. R. Luckhurst and G. W. Gray, editors (Academic Press, London, 1979), Chapter 4.
43. J. A. Pople, *Proc. Roy. Soc. (London)*, **A221**, 498 (1954).
44. M. E. Rose, "Elementary Theory of Angular Momentum" (Wiley, New York, 1957).
45. M. A. Cotter, *Mol. Cryst. Liq. Cryst.*, **39**, 173 (1977).
46. J. D. Rowell, W. D. Phillips, L. R. Melby and M. Panar, *J. Chem. Phys.*, **43**, 3442 (1965).
47. W. Maier and K. Markau, *Z. Phys. Chem. (N.F.)*, **28**, 190 (1961).
48. J. R. McColl and C. S. Shih, *Phys. Rev. Lett.*, **29**, 85 (1972).
49. H. C. Longuet-Higgins and B. Widom, *Mol. Phys.*, **8**, 549 (1964).
50. B. A. Baron and W. M. Gelbart, *J. Chem. Phys.*, **67**, 5795 (1977).
51. M. A. Cotter, Phil. Trans. Roy. Soc. (London), in press.
52. R. L. Humphries and G. R. Luckhurst, *Proc. Roy. Soc. (London)*, **A352**, 41 (1976).
53. See, for example, B. W. van der Meer and G. Vertogen, in "The Molecular Physics of Liquid Crystals", G. R. Luckhurst and G. W. Gray, editors (Academic Press, London, 1979), Chapter 6 and references therein.
54. W. L. McMillan, *Phys. Rev. A (a)*, **4**, 1238 (1971); (b) **8**, 1928 (1973).
55. R. J. Meyer and W. L. McMillan, *Phys. Rev. A*, **9**, 899 (1974); R. J. Meyer, *Phys. Rev. A*, **12**, 1066 (1975).
56. G. E. Feldkamp, M. A. Handschy and N. A. Clark, *Phys. Lett.*, **85A**, 359 (1981).

57. S. Chandrasekhar, K. L. Savithramma and N. V. Madhusudana, "Extension of McMillan's Model to Liquid Crystals of Disc-Like Molecules", preprint.
58. G. R. Luckhurst and B. A. Timimi, *Mol. Cryst. Liq. Cryst. (Lett)*, **64**, 253 (1981).
59. C. Zannoni and M. Guerra, *Mol. Phys.*, **44**, 849 (1981); G. R. Luckhurst and P. Simpson, *Mol. Phys.*, **47**, 251 (1982); and references therein.
60. See, for example, H. C. Anderson, D. Chandler, and J. D. Weeks, *Adv. Chem. Phys.*, **34**, 105 (1976).
61. C. S. Shih and R. Alben, *J. Chem. Phys.*, **57**, 3055 (1972).
62. W. M. Gelbart and B. Barboy, *Mol. Cryst. Liq. Cryst.*, **55**, 209 (1979); *Accts. Chem. Res.*, **13**, 290 (1980).
63. E. Praestgaard and J. Rotne, *Chem. Phys.*, **24**, 125 (1977).
64. J. Shen, Lin Lei, L. Yu and C-W Woo, *Mol. Cryst. Liq. Cryst.*, **70**, 301 (1981).
65. Th. W. Ruijgrok and K. Sokalski, *Physica*, **111A**, 45 (1982).
66. J. Corner, *Proc. Roy. Soc. (London)*, **A192**, 275 (1978).
67. B. Barboy and W. M. Gelbart, *J. Chem. Phys.*, **71**, 3053 (1979); *J. Stat. Phys.*, **22**, 709 (1980).
68. For a discussion of the use of van der Waals and hard-rod theories to treat nematogenic solutions, see D. E. Martire in "The Molecular Physics of Liquid Crystals", G. R. Luckhurst and G. W. Gray, editors (Academic Press, London, 1979), Chapter 11.
69. M. A. Cotter and D. C. Wacker, *Phys. Rev. A*, **18**, 2669; 2676 (1978).
70. W. M. Gelbart and A. Ben-Shaul, *J. Chem. Phys.*, **77**, 916 (1982).
71. K. L. Savithramma and N. V. Madhusudana, *Mol. Cryst. Liq. Cryst.*, in press.