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On the Form of the Free Energy for Uniaxially Ordered Liquids†

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We use the generalized van der Waals theory to derive forms of the Helmholtz free energy $\bar{F}$ for orientationally ordered liquids composed of rod-like molecules. The theoretically derived density and temperature dependences of $\bar{F}$ are compared with those assumed in current phenomenological descriptions, and used to discuss the competing roles of intermolecular attractions and repulsions. Successively higher order angle dependences in the mean attraction and packing entropy contributions to $\bar{F}$ are considered. Contrary to recent suggestions from phenomenological analyses, these corrections are argued to *increase* the discrepancy between theoretical and measured values of the orientational order parameter, transition temperature, etc. We then present the results of computations on the thermodynamic properties of a fluid of asymmetric ellipsoidal particles, all of whose axes are different. It is concluded that the relative stability of the nematic phase, and hence the strength of the first-order phase transition, is significantly exaggerated by failing to take into account deviations from cylindrical molecular symmetry.

I INTRODUCTION

Since the pressure-dependent experimental studies of Deloche, Cabane and Jerome,[1] and of McColl and Shih,[2] considerable attention has been focused on the competition between intermolecular repulsions and attractions in determining the stability of nematic liquid-crystalline phases. Much of this discussion[1–5] has been based on the following phenomenological expression

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for the Helmholtz free energy (writing only f-dependent terms):

$$\bar{F} = -\tfrac{1}{2}g\eta^2 - T\bar{S}_{\text{mixing}}. \tag{1}$$

Here η is the usual order parameter,

$$\eta = \langle P_2(\cos\theta)\rangle = \int_{-1}^{+1} \mathrm{d}(\cos\theta)P_2(\cos\theta)f(\cos\theta); \tag{2}$$

$f(\cos\theta)$ denotes the fraction of molecules (assumed cylindrically symmetric) whose long axes make an angle θ with respect to a space-fixed axis, and $P_2(\cos\theta)$ is the second Legendre polynomial.

$$\bar{S}_{\text{mixing}} = -k\int_{-1}^{+1} \mathrm{d}(\cos\theta)f(\cos\theta)\ln f(\cos\theta) \tag{3}$$

is the "entropy of mixing" ("orientational entropy"), and g is a phenomenological quantity whose explicit dependence on temperature and density is yet to be specified.

Assuming g to be a linear function of temperature,

$$g = A(\rho) + TB(\rho), \tag{4}$$

the A and BT terms have been identified[1-5] with the internal energy and "packing" entropy contributions to $\bar{F}$ from the van der Waals attractions and steric repulsions respectively. McColl and Shih[2] have suggested in particular how an experimental value for the ratio $\chi = BT/(A + BT)$ can be obtained from constant density measurements of η vs. T. They found that $\chi \approx 0.45$, and thereby concluded that "steric and energetic effects each contribute about equally to molecular alignment."[2]

Equation (1) has also been studied from a very different point of view, in which no explicit reference is made to repulsive forces. Here[6,7] g is assumed to depend only on the density, e.g., via a simple power law: $g = g(\rho) = g^{(0)}\rho^n$. It is found in this case that Eq. (1) fails to explain quantitatively much of the $\eta(T)$ data for nematics. Substantial improvement is obtained by subtracting from (1) a term $\frac{1}{2}h\langle P_4(\cos\theta)\rangle$ associated with higher order angle dependence in the intermolecular potential[6-9]—here P_4 is the fourth Legendre polynomial and h is an empirically determined quantity. Better agreement with experiment is also gotten by including a term arising from deviations of the molecular shape from cylindrical symmetry.[10]

In the present note we consider derivations of Eq. (1) and its extensions, in an effort to expose the assumptions about molecular interactions on which they are based. We use these results to discuss critically the several conclusions which have been drawn recently about the relative importance of attractions vs. repulsions, and of rod-like vs. plate-like molecular symmetry. Mean field coupling between anisotropic repulsions and attractions is shown to complicate significantly the separation of "steric" and "energetic" effects. Computational results are presented for the thermodynamic properties of fluids whose constituent particles are hard, asymmetric ellipsoids. We find that the discontinuities associated with the isotropic-nematic phase transition are very sensitive to small deviations from axial (e.g., rod-like) symmetry.

II $P_2(\cos\theta)$—THEORY FOR ROD-LIKE MOLECULES

A Generalized van der Waals description

The generalized van der Waals (GVDW) theory has recently been formulated[11–13] to account for the competing roles of attractions and repulsions in determining the structure of simple liquid crystals. In this approach the total interaction energy is assumed pairwise additive and the pair potential is written as the sum of a "hard core" repulsion $v_{\text{h.c.}}$ and a "smooth" attraction v_{attr}, each depending on the center-of-mass separation $\mathbf{r}$ and on the individual molecular orientations Ω and Ω':

$$\begin{aligned} V_{\text{total}}(\mathbf{r}_1\Omega_1, \ldots, \mathbf{r}_N\Omega_N) &= V_{\text{h.c.}} + V_{\text{attr}} \\ &= \sum_{i<j} v_{\text{h.c.}}(\mathbf{r}_{ij}, \Omega_i\Omega_j) + \sum_{i<j} v_{\text{attr}}(\mathbf{r}_{ij}\Omega_i\Omega_j). \end{aligned} \tag{5}$$

The contributions of $v_{\text{h.c.}}$ are treated as exactly as possible, thereby including in an approximate way the short-range positional and orientational order due to the intermolecular shape repulsions. The attractions v_{attr}, on the other hand, enter only through a mean-field averaging. Specifically, the attraction contribution to the interaction energy appearing in the many-body configuration integral is replaced [see, for example, Ref. 12(b)] by its average:

$$\begin{aligned} V_{\text{attr}}(\mathbf{r}_1\Omega_1, \ldots, \mathbf{r}_N\Omega_N) &\to \frac{N}{2}\rho \int \mathrm{d}\,\Omega \bar{f}(\Omega) \int \mathrm{d}\,\Omega' \bar{f}(\Omega') \int \mathrm{d}\mathbf{r} v_{\text{attr}}(\mathbf{r}, \Omega\Omega') g(\mathbf{r}\Omega\Omega') \\ &\equiv \frac{N}{2} \int \mathrm{d}\Omega \bar{f}(\Omega) \Psi_{\text{attr}}(\Omega). \end{aligned} \tag{6}$$

Here $\bar{f}(\Omega)$ is the orientational distribution function $[=(\frac{1}{2}\pi) f(\cos\theta)$ for axially symmetric particles] and g is the two-body radial distribution function.

$$\Psi_{\text{attr}}(\Omega) = \rho \int \mathrm{d}\Omega' f(\Omega') \int \mathrm{d}r v_{\text{attr}}(\mathbf{r}, \Omega\Omega') g(\mathbf{r}\Omega\Omega') \tag{7}$$

is the effective attraction, or "mean field" felt by each molecule. It then follows[11,12] that the $\bar{f}$-dependent terms in the Helmholtz free energy per particle can be written as

$$\bar{F} = \frac{1}{2}\int d\Omega \bar{f}(\Omega)\Psi_{\text{attr}}(\Omega) + kT\int d\Omega \bar{f}(\Omega)\ln \bar{f}(\Omega) + \Delta\bar{F}_{\text{h.c.}}[\bar{f}(\Omega)] \tag{8}$$

$\Delta\bar{F}_{\text{h.c.}}$ is the excess (over that of an ideal gas) free energy of a fluid of hard particles which interact via $v_{\text{h.c.}}$ and whose orientational distribution is given by $\bar{f}(\Omega)$.

Two practical problems arise immediately. First, it is extremely difficult to obtain accurate results for the analytical functional dependence of $\Delta\bar{F}_{\text{h.c.}}$ on $\bar{f}(\Omega)$. For the case of hard cores which are spherocylindrical in shape, scaled particle theory has been used[11,12] to derive approximate expressions for $\Delta\bar{F}_{\text{h.c.}}[\bar{f}(\Omega)]$. Second, the radial distribution, $g(\mathbf{r}, \Omega\Omega')$ is a tremendously complicated, essentially unknown, function for liquid-density fluids composed of very anisotropic hard particles. A most natural approximation, then, is to replace g by the Boltzmann factor involving $v_{\text{h.c.}}$:

$$g(\mathbf{r}\Omega\Omega') \rightarrow \exp\left[-\frac{1}{kT}v_{\text{h.c.}}(\mathbf{r}, \Omega\Omega')\right]. \tag{9}$$

This choice ignores g's dependence on the density, but preserves the "guts" of the short-range positional and orientational correlations due to the molecular shape repulsions.

Using scaled particle theory to evaluate $\Delta\bar{F}_{\text{h.c.}}$ for hard spherocylinders, and Eq. (9) for g, we have that

$$\bar{F} = \frac{1}{2}\int d\Omega \bar{f}(\Omega)\Psi_{\text{attr}}(\Omega) + kT\int d\Omega \bar{f}(\Omega)\ln \bar{f}(\Omega) + \lambda kT\int d\Omega \times \int d\Omega' f(\Omega)f(\Omega')|\sin \sphericalangle(\Omega, \Omega')| \tag{10}$$

where $\sphericalangle(\Omega, \Omega')$ is the angle between the long axes of the two molecules, and

$$\Psi_{\text{attr}}(\Omega) = \rho\int d\Omega' \bar{f}(\Omega')\int' d\mathbf{r}\, v_{\text{attr}}(\mathbf{r}, \Omega\Omega'). \tag{11}$$

The prime on the $\mathbf{r}$-integral restricts $\mathbf{r}$ to those values for which the hard cores, with orientations Ω and Ω', do not penetrate each other. Finally λ is a function of the number density and of the hard rod size and shape: from Cotter's scaled particle theory[12] we have, for example,

$$\lambda = 12(R-1)^2 v_0\rho[1 - v_0\rho(3R-3)/3(3R-1)]/\pi(3R-1)(1-v_0\rho)^2. \tag{12}$$

Here $v_0 = \pi D^3/6 + \pi D^2 L/4$ is the volume of the spherocylindrical core of diameter D and height $L + D$; $R = (L + D)/D$ is its length-to-width ratio.

Equation (10) can be rewritten as follows. The second term is simply $-T$ times $\bar{S}_{\text{mixing}}$. The third is an entropy contribution from the anisotropic repulsions [it vanishes—see Eq. (12)—as $R \rightarrow 1$]. Finally, the first term is the mean attraction "contaminated" by the prime in Eq. (11), i.e., by the hard core excluded volume condition. Now, it has been shown [11(b)], that $\Psi_{\text{attr}}(\Omega) = \Psi_{\text{attr}}(\cos\theta)$ can be expressed to a good approximation in the form

$$-|\Psi_0|\rho - |\Psi_2|\rho\eta P_2(\cos\theta) \tag{13}$$

where Ψ_0 and Ψ_2 are ρ- and T-independent quantities determined completely by the dispersion coefficients characterizing the intermolecular attraction, and by L and D defining the hard core repulsions. Thus the first term in Eq. (10) becomes $-\frac{1}{2}\rho|\Psi_0| - \frac{1}{2}\Psi_2|\eta^2$. Furthermore, if $\sin \sphericalangle (\Omega, \Omega')$ is expanded in a Legendre series and only the first two terms retained, the third term in (10) can be expressed as $\pi\lambda kT(1 - 5\eta^2/8)/4$. Thus the f-dependent part of the free energy $\bar{F}$ takes the form of Eq. (1) where $g = \mathrm{A} + BT$ with:

$$A = \rho|\Psi_2| \tag{14A}$$

and

$$B = \frac{5\pi}{16} k\lambda \approx k\lambda. \tag{14B}$$

B is indeed independent of the temperature, and varies with density via λ—it becomes proportional to R for $R \gg 1$, as had been assumed in Ref. [4]. A is also T-independent, and it goes as ρ^{+1} instead of the usually asserted ρ^{+n} with $n = 2, 3$ or 4.

B Maier-Saupe-Luckhurst description

Note that in the GVDW theory the pair intermolecular interaction is divided up into repulsions and attractions, the former being treated as exactly as possible and only the latter being mean-field averaged. In the theoretical approach of Luckhurst and his collaborators,[6, 7, 10] on the other hand, the entire pair potential is mean-field averaged. For rod-like molecules, for example, they write

$$v_{\text{pair}}(r; \theta_1\phi_1; \theta_2\phi_2) = 4\pi \sum_{L_1, L_2, n} U_{L_1L_2;n}(r) Y_{L_1n}(\theta_1\phi_1) Y^*_{L_2n}(\theta_2\phi_2) \tag{15}$$

where the Y_{Ln}'s are the spherical harmonics and $\theta_1\phi_1$ give the polar and azimuthal angles of the long axes of "1" relative to the center-of-mass separation vector (and of course the same for "2"). Assuming only radial dependence for the pair correlation function, v_{pair} is then averaged separately over r, Ω_r and Ω_2. This gives the effective one-body potential:

$$\Psi(x) = \bar{U}_0 + \bar{U}_2 \eta P_2(x) + \cdots \tag{16}$$

Here $P_{n \geq 4}(x)$ terms have been suppressed, and

$$\bar{U}_L = 4\pi\rho \int \mathrm{d}r r^2 g(r) \left[\sum_n U_{LL:n}(r) \right], \; L = 0, 2, \ldots, \tag{16A}$$

where $g(r)$ is the radial distribution function. Writing

$$f(x) \equiv \exp[-\Psi(x)/kT] \Big/ \int_{-1}^{+1} \mathrm{d}x \exp[-\Psi(x)/kT],$$

and the thermodynamic internal energy and entropy as

$$\frac{1}{2} \int_{-1}^{+1} \mathrm{d}x f(x) \Psi(x) \equiv \bar{V} \quad \text{and} \quad -k \int_{-1}^{+1} \mathrm{d}x f(x) \ln f(x) \equiv \bar{S}_{\text{mixing}},$$

the Helmholtz free energy assumes immediately the form of Eq. (1) with $g = -\bar{U}_2$:

$$\bar{F} = \bar{V} - T\bar{S}_{\text{mixing}} = -\tfrac{1}{2}(-\bar{U}_2)\eta^2 - T\bar{S}_{\text{mixing}}. \tag{17}$$

In order that the above expression for $\bar{F}$ be thermodynamically self-consistent, it must yield identical results for the entropy $\bar{S}$ from both $\bar{S} \equiv -\partial \bar{F}/\partial T$ and $\bar{S} \equiv \bar{V} - \bar{F}/T$. It follows that U_2 cannot depend explicitly on the temperature. Luckhurst *et al.*[6,7] have suggested further that $\bar{U}_L$ depends on density according to a simple power law:

$$\bar{U}_L = \bar{U}_L^{(0)} \rho^n. \tag{18}$$

Hence $B \leftrightarrow 0$ and $A \leftrightarrow -\bar{U}_2^{(0)}\rho^n$ in Eq. (4). Use of the corresponding $\Psi(x) = \bar{U}_0^{(0)}\rho^n + \bar{U}_2^{(0)}\rho^n \eta P_2(x) + \cdots$ in

$$\eta \equiv \int_{-1}^{+1} \mathrm{d}x P_2(x) e^{-\Psi(x)/kT} \Big/ \int_{-1}^{+1} \mathrm{d}x e^{-\Psi(x)/kT} \tag{19}$$

allows the quantity $-\rho(\partial\eta/\partial\rho)_T / T(\partial\eta/\partial T)_\rho \equiv \gamma$ to be evaluated: γ is found to equal n. But from the McColl and Shih measurements[2] we know that $\gamma = 4.0 \pm 0.1$ for para-azoxyanisole (PAA). Thus Luckhurst *et al.*[7] set $n = 4$ and argue that this corresponds to $1/r^{12}$ distance-dependence for the pair potential. There is, however, no sound basis for this often quoted [see, for example, the discussion in Ref. 15(c)] correspondence between $1/r^{3n}$ pair potentials and ρ^n mean field averages. In any case, explicit temperature dependence for g, arising from hard core repulsions in the GVDW formulation of $\bar{F}$, makes invalid the relation $\gamma = n$. In the calculations of

Baron and Gelbart[11(b)] and of Cotter,[12(a)] for example γ was found to be ≈ 4 even though the density dependence of A and B is much weaker than ρ^4.

More generally, there is a fundamental difference between the GVDW and the Maier–Saupe–Luckhurst (MSL) mean field formulations of liquid crystal thermodynamics. This is most clearly seen by considering their respective treatments of a system whose interaction potential can be written in the form of Eq. (5). Then the MSL effective potential involves an average of v_{attr} only, over an approximate pair correlation function—much as the GVDW Ψ is defined by average of v_{attr} over $\exp(-v_{\text{h.c.}}/kT)$. [In fact, a potential of the form (5) has not been considered by Luckhurst *et al.* Such a choice is not natural to their approach since it precludes the possibility of mean field averaging the *full* pair interaction, including ("soft") repulsions. We mention it here only to dramatize the difference between their approach and ours, and—in particular—to expose the source of the T-dependent term in g.] The essential difference comes from comparing [cf. Eqs. (8) and (17)]

$$\bar{F}_{\text{MSL}} = \bar{V} - T\bar{S}_{\text{mixing}} \tag{20}$$

with

$$\bar{F}_{\text{GVDW}} = \bar{V} - T\bar{S}_{\text{mixing}} + \Delta\bar{F}_{\text{h.c.}}[\bar{f}(\Omega)]. \tag{21}$$

As argued above, $\bar{V}$ does not depend explicitly on temperature. Nevertheless, in Eq. (8) there is explicit T-dependence in $\bar{F}$, beyond that arising from $-T\bar{S}_{\text{mixing}}$. Recall that $\Delta\bar{F}_{\text{h.c.}}$ is defined by

$$\Delta\bar{F}_{\text{h.c.}} = -\frac{kT}{N}\ln\int \mathrm{d}r^N \exp\left[\frac{-V_{\text{h.c.}}(r^N, \bar{f}(\Omega))}{kT}\right]. \tag{22}$$

Thus $\Delta\bar{F}_{\text{h.c.}}$ is proportional to T. Applied to spherocylinders, for example, we have seen that $\Delta\bar{F}_{\text{h.c.}} = T[\lambda k\int \mathrm{d}\Omega\int \mathrm{d}\Omega' \bar{f}(\Omega)\bar{f}(\Omega')\sin \sphericalangle (\Omega,\Omega')]$. This is the source of $B \not\equiv 0$ and explicit temperature dependence for g in the GVDW formulation.

C Contact with experiment

We are now in a position to estimate a theoretical value for the ratio $\chi \equiv BT(A + BT)$. As mentioned earlier, χ has been interpreted[1–4] as defining the relative importance of the intermolecular repulsions in determining the stability of the nematic phase. The classic theory of Maier and Saupe,[15] and its extension by Luckhurst *et al.*[6,7] correspond to a limiting case of the GVDW theory† in which the hard rod core reduces to a sphere.

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† As the hard rod core reduces to a sphere in the GVDW theory we recover [11(a)] all of the Maier–Saupe results, but with $A \sim \rho$ instead of their assumed ρ^2 dependence.

That is $R \to 1$ and λ [Eq. (12)] $\to 0$, or more generally—$\Delta\bar{F}_{\text{h.c.}}[\bar{f}(\Omega)] \to 0$. Thus $B = 0$ and $\chi = 0$: the repulsions play no explicit role in the nematic ordering. In the limit of vanishing attractive forces, on the other hand, $A = 0$ and $\chi = 1$. Indeed, then, χ appears to define the relative importance of the anisotropic repulsions *vs.* attractions.

There is, however, a problem in assinging additive terms in thermodynamic functions to separate contributions from attractions and repulsions. Consider again Eq. (11) for the effective attraction. Even if v_{attr} is taken to be purely isotropic, e.g., $v_{\text{attr}} = -C_{\text{iso}}/r^6$, $\Psi_{\text{attr}}(\cos\theta)$ still depends on angle. For $R = 3$, for example, we find [11(b)] that $\Psi_{\text{attr}}(x)$ has the form (13) with $|\Psi_2|/|\Psi_0| \approx 0.2$: Thus $A = \rho|\Psi_2| > 0$, instead of the zero value which obtains in the case of spherical repulsions. This situation arises from the prime on the **r**-integral in Eq. (11)—it is the pair excluded volume condition, i.e., the short-range orientational ordering due to molecular shape repulsions, which introduces angles dependence into the *mean* field even when there is none in the *pair* attraction. [There are also, of course, *an*isotropic terms (e.g., $-C_{an}\cos^2 \sphericalangle (\Omega, \Omega')/r^6$) in v_{attr} which give additional contributions to $|\Psi_2|/|\Psi_0|$]. Thus the effective attraction $\Psi(\cos\theta)$ is "contaminated" by repulsion effects and we cannot speak of the $-\frac{1}{2}A\eta^2$ in $\bar{F}$ as being purely attractive in origin. Nevertheless, it is worthwhile to keep track, *via* say the GVDW theory, of the various contributions to thermodynamic properties from intermolecular attractions and excluded volume effects. This kind of microscopic basis for liquid anisotropy has already been used in preliminary attempts[3,11] to explain variations of the isotropic-nematic transition temperatures through homologous series.

In the case of a typical liquid-crystal forming molecule such as PAA, which is both rod-like *and* plate-like, the steric repulsions can only crudely be modeled by a hard sphero-cylinder interaction. The choice of a length-to-width ratio is correspondingly arbitrary: usually a value of 3 is chosen[16,12(a)] for $R = (L + D)/D$. With $v_0\rho = (230\ \text{Å}^3[16])(2.7 \times 10^{-3}/\text{Å}[2]) = 0.64$, this value of R leads to—see Eq. (12)—$\lambda \approx 8.5$. In the Appendix we show how an *a priori* estimate of the mean attraction gives $A = \rho|\Psi_2| \approx 6.6 \times 10^{-13}$ erg, as compared to $BT_{408°\text{K}} \approx \lambda kT_{408°\text{K}} \approx 4.9 \times 10^{-13}$ erg. Thus the theoretically determined value of χ is $\chi_{\text{PAA rod}}(T = 408°\text{K}, \rho = 2.7 \times 10^{-3}/\text{Å}^3) \approx 0.43$.

The data of McColl and Shih provide an experimental value for χ in the following way. At the fixed density $\rho = 2.7 \times 10^{-3}/\text{Å}^3$, they measured η over the full thermal range (390°K to 437.5°K) of nematic PAA. Thus we have a set of (η, T) couples for each temperature in this range. But from the minimization of Eq. (1) with respect to $f(\cos\theta)$ we obtain as set of (η, g/kT) —couples for all $g/kT \geq 4.54$—see, for example, Table 1 of Ref. [15(b)]. These two sets of data allow us to associate a value of g with each T, and

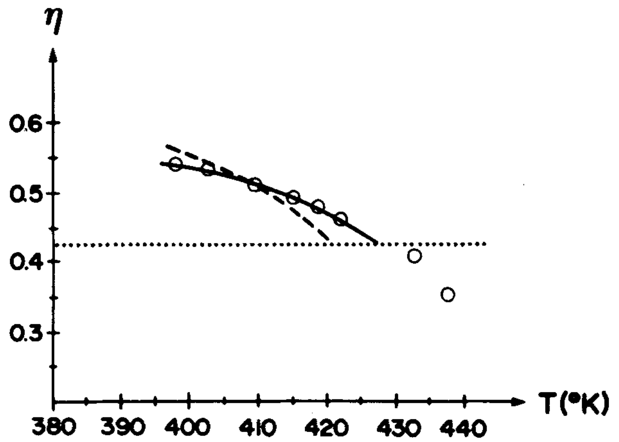

FIGURE 1 Order parameter, η, vs. temperature, T, at fixed density. Open circles show the experimental data obtained by McColl and Shih[2] for PAA at a fixed density of 2.7×10^{-3} molecules/Å^3. The solid curve corresponds to the analysis described in the text, in which g is assumed to have the form $A + BT$; the dashed curve shows the result of assuming g to be independent of T.

hence to determine a single pair of values of A and B, *if* $g(T)$ is sufficiently linear. $g(T)$ does indeed appear to be linear, at least within the accuracy with which we can read the published plot of constant-density $\eta(T)$ data—see McColl and Shih's Figure 1. The average slope of g/k *vs.* T gives $B/k \approx 2.1$; with $g/k(T = 408°\mathrm{K}) \approx 1907°\mathrm{K}$ this yields $\chi(T = 408°\mathrm{K}) \approx 0.45$.[2]

We can in fact use $g = A + BT/k$ *vs.* T, inferred as above from experiment, to compute a set of constant-density (η, T)-couples from the tabulated η *vs.* g/kT solution[15(b)] to the minimization of $\bar{F}$, Eq. (1). These results are shown by the solid curve in Figure 1; the open circles are the experimental data of McColl and Shih. The dashed curve shows $\eta(T)$ computed in the same way but with $g(T)$ replaced by its average [g(average)/$k \approx 1910°\mathrm{K}$]—this corresponds to the Maier–Saupe theory, where the anisotropic repulsions are neglected and $A(\approx g)$ is assumed to be independent of temperature. A plot of $\eta(T)$ based on our g_{GVDW} would lie much too high since $g = A_{\mathrm{GVDW}} + B_{\mathrm{GVDW}}T$ is several times too big. Cotter's[12(a)] lies less high than ours—see her Figure 2—since she evaluates B at a lower density (0.45 *vs.* 0.64) and pick an *ad hoc* A value which is four times smaller than our $A_{\mathrm{GVDW\,PAA}}$.

Figure 1 is to be compared with Figure 1 of Ref. [2]; the latter shows the same data (open circles) and solid and dashed curves computed from Eq. (1), presumably as described above. The most significant feature of our Figure 1 is that the solid and dashed $\eta(T)$'s stop at $\eta = 0.43$: Eq. (1), as is well known, predicts a *universal* value of 0.43 for the *minimum* order parameter

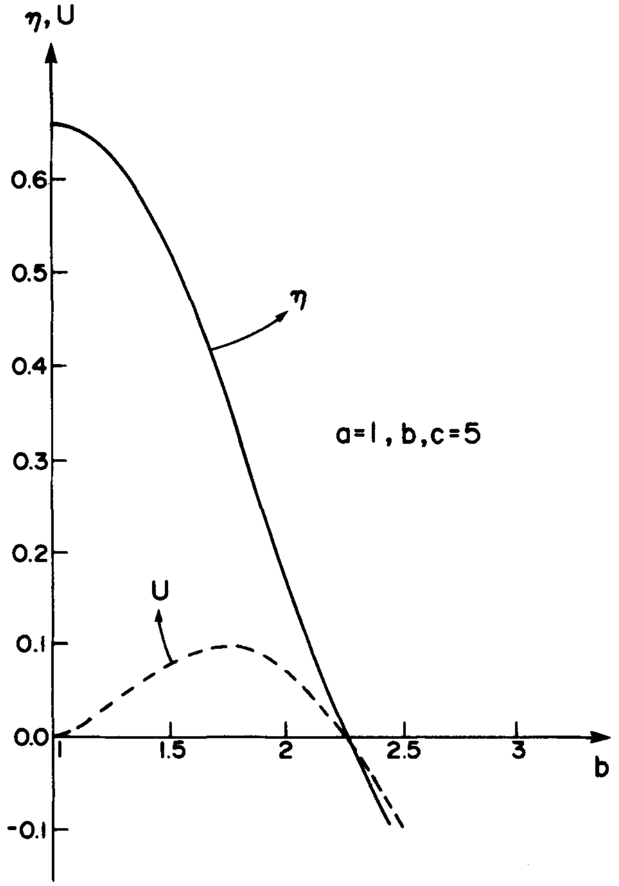

FIGURE 2 $\eta = \langle P_2(\cos\theta)\rangle$ and $U = \langle D^{(2)}_{0,2}(\Omega)\rangle$ vs. b, computed for a hard-ellipsoid liquid from the Lasher (six orientation) equations of state. b is the length of the middle axis of an $(a = 1) \times b \times (c = 5)$ ellipsoid.

—*regardless of the form of g.* (See also the discussion in Ref. [8].) Thus a principal conclusion that must be drawn from the McColl and Shih measurements is that the form given by Eq. (1) for the free energy is inadequate. Equation (1) simply cannot explain the experimental values of $\eta < 0.43$ observed at the upper end of the thermal range for many nematic liquids.

From the discussion in Section IIA we have seen how Eq. (1) follows from a $P_2(\cos\theta)$-level truncation of the GVDW and MSL mean field theories applied to liquids of rod-like particles. In part III below we consider $P_4(\cos\theta)$ corrections, and in IV we treat the case of lower-than-axial particle symmetry.

III $P_4(\cos\theta)$ CORRECTIONS FOR ROD-LIKE PARTICLES

Equation (1) was derived from Eq. (10) upon dropping the P_4 and higher-order contributions to $\Psi_{\text{attr}}(x)$ and $\sin \measuredangle (\Omega, \Omega')$. Retaining the P_4 terms allows (10) to be written as

$$\bar{F} = -\tfrac{1}{2}g\eta^2 - \tfrac{1}{2}h\xi^2 + kT\int_{-1}^{+1} dx f(x) \ln f(x) \qquad (23)$$

where

$$g = \rho|\Psi_2| + \frac{5\pi}{16}\lambda kT \quad \text{as before} \qquad (23A)$$

$$h = \rho|\Psi_4| + \frac{9\pi}{128}\lambda kT, \qquad (23B)$$

and

$$\xi \equiv \langle P_4(\cos\theta)\rangle = \int_{-1}^{+1} dx f(x) P_4(x). \qquad (23C)$$

$|\Psi_L|$ is defined by the expansion $\Psi(x) = -\rho\sum_{L=0}^{\text{even}}|\Psi_L|\langle P_L\rangle P_L(x)$. Minimization of $\bar{F}$ with respect to $f(x)$ now leads to two coupled equations for η and ξ, involving the two dimensionless quantities g/kT and h/kT. The smallest non-zero solution for η is no longer 0.43, but depends instead on the ratio h/g.

Using Eq. (12) for λ, and earlier *a priori* calculations[11(b)] for $|\Psi_2|$ and $|\Psi_4|$, we find for $R = 3$ that g/h is positive and is approximately equal to two. In fact g/h is positive for *any* spherocylindrical rod, independent of R. But when g and h have the same sign, the coupled self-consistency equations for η and ξ lead to a minimum η which is greater than 0.43, in increasing discrepancy with experiment for prototype systems such as PAA. For example, in the GVDW calculations of Baron and Gelbart[11(c)] all P_4 (and higher order) contributions to $\bar{F}$ were included since both the $\Psi_{\text{attr}}(\Omega)$ given by (11) and the $\langle\!\langle \sin \measuredangle (\Omega, \Omega')\rangle\!\rangle$ appearing in (10) were computed directly, without expansion in Legendre series. If the ensuing thermodynamic equations were then solved exactly, their values of η—as well as other discontinuities of the first-order phase transition (e.g., entropy change, density difference, etc.)—would be greater than those of Cotter's calculations[12(a)] in which only the P_2-contributions were included. (The same is true of the original form of Maier–Saupe theory,[15] in which again only P_2-contributions are involved.) [In fact, the main reason that Baron and Gelbart find much greater discontinuities than Cotter is because they constrain $f(\cos\theta)$ to have a specific functional form (see Ref's. 11b, 11c, 12a and 18 for a discussion of this point).]

In the Luckhurst *et al.* theory, summarized by Eq. (20) and

$$\bar{V} = \frac{1}{2}\int_{-1}^{+1} \mathrm{d}x f(x)\Psi(x), \tag{24}$$

and

$$\Psi(x) = \sum_{n=0}^{\text{even}} \bar{U}_L \langle P_L(x)\rangle P_L(x), \tag{25}$$

$$f(x) = \exp[-\Psi(x)/kT] \bigg/ \int_{-1}^{+1} \mathrm{d}x \exp[-\Psi(x)/kT], \tag{26}$$

the quantities g and h reduce to $-\bar{U}_2$ and $-\bar{U}_4$. But the $\bar{U}_L$'s have not been calculated: they are defined—cf. Eq. (16A)—in terms of an *isotropic* $g(r)$ which represents too drastic an approximation to the true pair correlations. Luckhurst *et al.* have treated g and h as empirical parameters and varied them so that the coupled equations for η and ξ give solutions in best agreement with experiment. They found,[7] for example, that a value of $g/h \approx -4$ allows the constant-density $\eta(T)$ data[2] for PAA to be fit very well. But recall that a negative value of g/h does not appear when the mean attraction for rod-like molecules is computed *via* the GVDW theory.

The above facts suggest that the problem might lie not in the convergence of the Legendre polynomial expansions, nor in the mean field approximation, but rather in the choice of shape for the molecular cores. This conclusion is corroborated by the work of Luckhurst *et al.*[10] who, using the same mean-field-averaging of the full pair potential as described above, but now with nonaxial molecular symmetry, find a one-body effective interaction which has the form $aP_2(\theta) + bD^{(2)}_{0,2}(\theta, \phi)$. Here $D^{(2)}_{0,2}(\theta, \phi)$ is the 0,2-element of the second rank Wigner rotation matrix, $a = C_{200}\langle P_2(\theta)\rangle + 2C_{220}\langle D^{(2)}_{0,2}(\theta, \varphi)\rangle$, $b = 2aC_{220}/C_{200}$, and C_{200} and C_{220} are defined by averages of the radial components of the pair potential. Again, treating the ratio C_{220}/C_{200} as an empirical quantity, η is shown to decrease with increasing C_{220}/C_{200} (note that $C_{220}/C_{200} = 0$ means zero deviation from cylindrical symmetry) and to equal the measured value of 0.35 for $C_{220}/C_{200} \approx 0.2$. In the next section below we show how such deviations from cylindrical symmetry can be explicitly accounted for in *a priori* theory of the short-range molecular repulsions.

IV LOWER-THAN-CYLINDRICAL SYMMETRY

We treat the possibility that the orientational order in the nematic state is exaggerated by choosing a rod to represent the molecular shape. Consider a liquid of hard particles, each having lower than cylindrical symmetry.

We can take, for example, ellipsoids whose three principal axes (a, b, c) are different: $a < b < c$. The limits $a = b < c$ and $a < b = c$ recover the cylindrical symmetry corresponding to "rods" and "plates," respectively. Neglecting attractions for the moment, we determine the thermodynamic properties of the liquid of hard ellipsoids. As mentioned earlier, this can be done by an extension of the scaled particle theory developed originally to treat fluids of hard spheres.[14] For cylindrically symmetric shapes (e.g., spherocylinders) several versions of the scaled particle theory have been worked out for the isotropic-nematic phase transition.[18]

Lasher[19], for example, has shown that a reasonable approximation to the thermodynamic functions is gotten by keeping only those terms which are linear in the pair excluded volume. Thus for the pressure we can write

$$\frac{P}{kT} = \left(\frac{\rho}{1 - \rho v}\right) + \left(\frac{\rho}{1 - \rho v}\right)^2 \sum_n \sum_m x_n x_m S_{nm} \tag{27}$$

where v is the volume of each particle, and

$$V_{nm}^{\text{ex}} = 2(v + S_{nm}) \tag{28}$$

is the volume excluded to a particle with orientation n by another with orientation m. x_n gives the fraction of particles which have orientation n. [In the usual continuum limit, $x_n \to x(n) \leftrightarrow f(\cos \theta_n)/2\pi$ where f is the orientational distribution function defined earlier.] Similarly, for μ_n, the chemical potential of a particle with orientation n, we write

$$\frac{\mu_n}{kT} = \frac{Pv}{kT} + \ln\left(\frac{\rho}{1 - \rho v}\right)x_n + 2\left(\frac{\rho}{1 - \rho v}\right) \sum_m x_m S_{nm} \tag{29}$$

Finally, the Helmholtz free energy follows from

$$\frac{F}{N} = \mu - \frac{P}{\rho} = \sum_n \mu_n x_n - \frac{P}{\rho}. \tag{30}$$

Whereas S_{nm} is not known for noncylindrical hard cores having arbitrary orientations n and m, it is readily evaluated in cases where the principal axes of the particles are coincident with each other. Thus if we allow only the six orientations in which the principal axes of the particles are coincident with those of a space-fixed reference frame, S_{nm} can be evaluated for interesting non-axially symmetric shapes. Using S_{nm} for the above six orientations of a $a < b < c$ ellipsoids, Eq. (27) for the pressure, and Eqs. (30) and (29) for the Helmholtz free energy and chemical potential, we have searched for the isotropic-uniaxial phase transition.

Figure 2 shows our results for η_{trans} in the case $a = 1, c = 5$ and $a < b < c$. For $b = 1$, the rod limit, *only* nematic ordering is possible and η_{trans} is as large as 0.67. This consistent with all previous treatments[18] of fluids of cylindrically symmetric hard particles—the first-orderness of the I–N phase transition is over estimated. $\Delta\rho/\rho_{\text{nem}}$ is found to be as large as 0.06 in this case, approximately ten times the experimentally observed values. As b increases, the "rod" becomes more plate-like and η_{trans} and $\Delta\rho/\rho_{\text{nem}}$ decrease. There exists a special value of $b = b^*(=\sqrt{a \cdot c} \approx 2.3)$, in fact, where $\eta_{\text{trans}} = \Delta\rho = 0$. This is the point where the tendencies to form nematic and planar uniaxial states become equal and the first-orderness disappears. For $b > b^*$ the particles are more plate-like than rod-like and it is the short axes which tend to line up in the uniaxial phase, i.e., $\eta < 0$.

In Figure 2 is also shown the value (at the transition) of the secondary order parameter U.† Note that even though U is always small (<0.1) in the nematic phase, a small amount of noncylindrical symmetry suffices to lower significantly the values of η_{trans} and $(\Delta\rho/\rho_{\text{nem}})$. For example, $\eta_{\text{trans}}(\Delta\rho/\rho_{\text{nem}})$ drops from 0.67 (0.056) to 0.45 (0.021) to 0.21 (0.005) as b increases from 1 to 1.61 to 1.95. It appears that the real world of liquid crystals takes place just to the left of the zero in Figure 2. Prototype liquid crystal-forming molecules such as PAA are indeed more rod-like than plate-like—but the small deviation of their symmetry from cylindrical ($a < b < b^*$) gives rise to a distinctly weak first-order I–N transition.

The calculation described immediately above was based on the restriction of molecular orientations to those (six) whose principal axes lie along a space-fixed coordinate system. To check the sensitivity of the derived thermodynamics to this constraint, consider again the case of spherocylinders. Here the theory can be worked out explicitly for arbitrary ("continuum") orientations: indeed this corresponds precisely to the description of Lasher.[19] For length-to-width ratios of 2.05, 2.50 and 3.01 he found $\eta_{\text{trans}} = 0.576$, 0.592, and 0.610 (these values are obtained by interpolation from the results he reports for R = 1.93, 2.75 and 3.56). Restricting the spherocylinder axes to the space-fixed x-y-z directions, we find $\eta_{\text{trans}} = 0.56$, 0.59 and 0.62, respectively: the differences are as small as 1–3%. Thus we can expect the behavior described above to bear up qualitatively when we remove the restriction on molecular orientations. *Other* properties, such as ρ_{nem} and $\Delta\rho$, are much more sensitive to this restriction, and so we must proceed with caution in interpreting the present results.

To make contact with our earlier discussion, we write out here the form which $\bar{F}$ takes in the case of molecules having lower-than-cylindrical sym-

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† U is defined by $\langle D_{0,2}^{(2)}(\Omega)\rangle$, in contrast to $\eta \equiv \langle D_{0,0}^{(2)}(\Omega)\rangle$. Here $D_{m,n}^{(2)}(\Omega)$ is the m,nth component of the second rank Wigner matrix, introduced in the text at the end of Section III. U is proportional through factors of order unity, to the secondary uniaxial order parameter defined in Ref. [10], [23] and [25].

metry. For the isotropic and uniaxially ordered liquid states of particles with d_{2h} symmetry, we have

$$\bar{F} = -\tfrac{1}{2}g_{200}\eta^2 - \tfrac{1}{2}g_{220}\eta U - \tfrac{1}{2}g_{222}U^2 - T\bar{S}_{\text{mixing}}. \tag{31}$$

Each g_{lmn} has the form

$$g_{lmn} = A_{lmn}(\rho) + TB_{lmn}(\rho). \tag{32}$$

The B_{lmn}'s are determined by the excluded volume $V^{\text{ex}}(\Omega)$ associated with a pair of particles whose relative orientation is Ω. [$V^{\text{ex}}(\Omega)$ is the continuum limit of the V^{ex}_{nm} defined in Eq. (28).] The A_{lmn}'s arise from the mean field averaged attractions. For example, using the Lasher scaled particle theory[19] to describe the hard core reference system, the GVDW formulation leads to

$$\bar{F} = -T\bar{S}_{\text{mixing}} + y\int d\Omega_1\,\bar{f}(\Omega_1)\int d\Omega_2\,\bar{f}(\Omega_2)\frac{S(\Omega_{12})}{v} + \frac{1}{2}\int d\Omega\,\bar{f}(\Omega)\Psi_{\text{attr}}(\Omega) \tag{33}$$

Here Ψ_{attr} is the mean field averaged pair attraction and $S(\Omega)$ is the continuum limit of the earlier defined S_{nm}:

$$\frac{S(\Omega)}{v} = \frac{V^{\text{ex}}(\Omega)}{2v} - 1. \tag{34}$$

$$y \equiv \frac{v\rho}{1 - v\rho} \tag{35}$$

is the dimensionless quantity which plays a fundamental role in the thermodynamic description of hard particle fluids.[20] Expanding both $\Psi_{\text{attr}}(\Omega)$ and the pair excluded volume $V^{\text{ex}}(\Omega)$ in Wigner functions, and neglecting all contributions of rank three and higher, leads directly to (31) and (32) with $A \propto \rho$ and $B \propto y$.

For the computations reported above we have neglected the contributions to $\bar{F}$ from Ψ_{attr}, and allowed only six molecular orientations in evaluating the B's [e.g., $S(\Omega) \to S_{\text{km}}$, etc.]. Calculations of the A's from Ψ_{attr}, and the B-contributions from higher order terms in $y(S_{\text{km}})$, are quite complicated and will be treated in subsequent work.

V DISCUSSION

We collect here some of the most important facts emerging from the above discussion:

i) A free energy having the form of Eq. (1) implies a minimum value of 0.43 for η; measured values for η are commonly found[15(b)] to be lower.

ii) Generalized van der Waals (GVDW) theory applied to rod-like molecules leads to constant density $\eta(T)$ curves which lie considerably above the measured ones.

iii) The highest temperature T^* at which a fixed density nematic phase is stable, or metastable, obtained by minimizing Eq. (1) with respect to $f(x)$, leads to the well-known result $g(T^*) = 4.54\, kT^*$. (This was originally obtained by Maier and Saupe[15(a)], who neglected the anisotropic repulsions and took g to be T-independent.) With $g \rightarrow g(T) = A + BT$, and $B \approx k\lambda$, this implies $T^* = (A/k)/(4.54 - \lambda)$. Since λ, Eq. (12) is an increasing function of both R and ρ this means that T^* becomes infinite (*i.e.*, the nematic phase is predicted to be stable or metastable at all temperatures) as either R or ρ becomes large enough.†

iv) P_4- (and higher)-corrections to Eq. (1) can lower η, but only if they enter with a sign opposite to the P_2-terms; *a priori* estimates of the P_4-corrections for rod-like molecules suggest that they have the *same* sign.

v) Corrections to (1) due to molecular deviations from cylindrical symmetry lower η considerably below 0.43.

From (i) and (iii) we conclude (with others before us) that Eq. (1) is not an adequate free energy function for quantitative analyses of nematic thermodynamics. We assert in addition [see (ii) and (iv)] that higher-order angle dependences [involving $P_{n\geq 4}(\cos\theta)$] do not provide a self-consistent improvement of the situation.

We believe instead that the desired correction is associated with deviations from molecular cylindrical symmetry, as shown above and suggested earlier by Luckhurst *et al.*[10] and Shih and Alben.[21] This correction is consistent with Cotter having found[17] that a rod-like shape tends to overestimate the stability of the ordered phase, *e.g.*, that $R < 3$ gives GVDW results in better agreement with experimental data on PAA. It can explain as well, for example, the situation mentioned in (iii). Our preliminary calculations on liquids composed of hard *ellipsoids* show, for example, that ρ^*—the density above which the nematic becomes stable or metastable—increases dramatically as the molecular symmetry is lowered from axial. This conclusion is further supported by the other calculations,[21–23] employing widely disparate approximations, in which explicit introduction of lower-than-axial symmetry has been shown to significantly decrease the value of η (and other discontinuities) at the isotropic-nematic phase transition.

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† This is related to the fact that for the pure, hard rod, fluid, where no attractions are present, there is a critical density ρ^*—depending only on R—above which the nematic phase can exist (i.e. is stable or metastable); for $R = 2.4$, for example, $T^* \rightarrow \infty$ for $\rho^* \rightarrow \approx \rho_{\mathrm{PAA}}$ ($P = 1$ atm, $T = 398°\mathrm{K}$)!

The thermodynamic treatment of a liquid of nonaxial hard particles is especially difficult because of the impossibility of obtaining analytical results for the pair excluded volume associated with arbitrarily oriented particles of this kind. But work is now in progress on this problem, using a recently developed[20] equation of state for hard core reference systems. We expect that a GVDW theory referenced to a liquid of noncylindrically symmetric particles will yield a much higher ρ^*, and hence a lower η^* and a realistic T^*.

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Appendix

We estimate here the values of Ψ_0, Ψ_2 and Ψ_4 appearing in $\Psi(x) = -|\Psi_0|\rho - |\Psi_2|\rho\eta P_2(x) - |\Psi_4|\rho\xi P_4(x)$. First note that $\Psi_{\text{isotropic phase}} = \Psi_{\eta=0=\xi} = -|\Psi_0|\rho$; thus, for the internal energy per molecule of the isotropic state of the liquid, we can write $\bar{V}_{\text{liq}} = \frac{1}{2}\langle\Psi_{\text{iso}}\rangle f_{\text{iso}} = -\frac{1}{2}|\Psi_0|\rho$. The enthalpy change per molecule, when this liquid is vaporized, is given by $\Delta\bar{H}_{\text{vap}} = (\bar{V}_{\text{gas}} - \bar{V}_{\text{liq}}) + P(\bar{\mathscr{V}}_{\text{gas}} - \bar{\mathscr{V}}_{\text{liq}})$, where $\bar{\mathscr{V}}$ denotes the volume per molecule. But at $P = 1$ atm, the gas can be taken to be ideal, so that $\bar{V}_{\text{gas}} = RT$ and $\bar{\mathscr{V}}_{\text{gas}} = RT/P \ll \bar{\mathscr{V}}_{\text{liq}}$. Thus $\Delta\bar{H}_{\text{vap}} \approx -\bar{V}_{\text{liq}} + 2RT = \frac{1}{2}|\Psi_0|\rho + 2RT$. For PAA the measured value of $\bar{q}_{\text{p}}(=\Delta\bar{H}_{\text{vap}})$ at $T_{\text{vap}} \approx 500°$ K is 17.8 kcal/mole (see data cited in,[12(a)] implying $|\Psi_0|\rho \approx 2.2 \times 10^{-12}$ erg.)

To estimate the values of Ψ_2 and Ψ_4 we use the results obtained by Gelbart and Gelbart[11(b)] in their calculation of mean attraction energies for molecules interacting through spherocyclindrical hard cores and van der Waals dispersion forces. For $R = 3$, and for reasonable ratios of the anisotropic to isotropic contributions to the pair attraction, they found $|\Psi_2|/|\Psi_0| \approx 0.3$ and $|\Psi_4|/|\Psi_2| \approx \frac{1}{2}$. Thus $|\Psi_2|\rho \approx 6.6 \times 10^{-13}$ erg and $|\Psi_4|\rho \approx 3.3 \times 10^{-13}$ erg, as reported in the text.