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Orientation-averaged pair correlations in a molecular theory of nematic liquid crystals

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A molecular theory of nematic liquid crystals is presented in which the short-range spatial correlations are accounted for by an orientation-averaged pair correlation function. This results in a two-fold self-consistency scheme whose spatial description resembles that in the conventional theory of classical liquids and whose orientational description resembles a mean-field theory. Numerical calculations are made for a simple potential chosen to describe para-azoxyanisole (PAA). Among the properties calculated are the two-phase coexistence curve, the order parameter along the coexistence curve, temperature dependence of the order parameter at constant pressure, and volume change and latent heat at the isotropic-nematic transition. Comparison with experimental data is made. There are encouraging signs to warrant further investigation.

I. INTRODUCTION

In a molecular theory of liquid crystals, one begins by writing down a model potential that describes the interaction between a pair of molecules. By assuming cylindrical symmetry for the molecules, it can be shown[1] that the most general form of the potential will be a function of five scalar variables: r_{12}, $\hat{\Omega}_1\cdot\hat{r}_{12}$, $\hat{\Omega}_2\cdot\hat{r}_{12}$, $\hat{\Omega}_1\cdot\hat{\Omega}_2$, and $\hat{\Omega}_1\times\hat{\Omega}_2\cdot\hat{r}_{12}$, where $\vec{r}_i$ and $\hat{\Omega}_i$ denote the position and orientation of the ith molecule. $\hat{\Omega}_1\times\hat{\Omega}_2\cdot\hat{r}_{12}$ actually offers only a selection between two signs. It is associated strictly with the chiral contribution, and is responsible for the cholesteric phase. $\hat{\Omega}_1\cdot\hat{r}_{12}$ and $\hat{\Omega}_2\cdot\hat{r}_{12}$ break the symmetry between splay and bend on the microscopic level. In a recent paper[2] we showed that functions with these arguments can be constructed to account for anisotropic repulsions, thus giving rise to anisotropic macroscopic properties. In most molecular-theoretic calculations to date, only functions with arguments r_{12} and $\hat{\Omega}_1\cdot\hat{\Omega}_2$ appear in the interaction formula. In most[2-7] of our own work we have followed Kobayashi[8] and McMillan[9] in expressing the potential in the convenient, though hardly realistic, form:

$$v(1,2)=v_0(r_{12})+v_2(r_{12})P_2(\hat{\Omega}_1\cdot\hat{\Omega}_2)+v_4(r_{12})P_4(\hat{\Omega}_1\cdot\hat{\Omega}_2)\,, \tag{1}$$

where P_l denote Legendre polynomials. This will again be the case in the present paper.

Given density $\rho\equiv N/V$ and temperature T, statistical mechanics evolves from the partition function

$$Z=\int\exp\left(-\sum_{i<j}^{N}\frac{v(i,j)}{kT}\right)\,d\vec{r}_1\,d\hat{\Omega}_1\cdots d\vec{r}_N\,d\hat{\Omega}_N\,, \tag{2}$$

and the n-particle distribution functions

$$P^{(n)}(1,2,\ldots,n)=\frac{N!}{Z(N-n)!}\times\int\exp\left(-\sum_{i<j}\frac{v(i,j)}{kT}\right)\times d\vec{r}_{n+1}\,d\hat{\Omega}_{n+1}\cdots d\vec{r}_N\,d\hat{\Omega}_N\,. \tag{3}$$

Of particular interest to a system characterized by pairwise interactions are the one- and two-particle distribution functions $P^{(1)}(1)$ and $P^{(2)}(1,2)$. When only orientational order is of concern, we can write

$$P^{(1)}(1)\equiv P^{(1)}(r_1,\Omega_1)=P^{(1)}(\theta_1)\equiv\rho f(\theta_1) \tag{4}$$

and

$$P^{(2)}(1,2)\equiv P^{(1)}(1)P^{(1)}(2)g(1,2)=\rho^2 f(\theta_1)f(\theta_2)g(1,2)\,, \tag{5}$$

where θ_i measures the orientation of the ith molecule relative to the director (taken along the z axis). $f(\theta)$ provides a measure of the long-range order, while $g(1,2)$, a pair correlation function, describes the short-range order in the system.

In the Maier-Saupe form of the mean field theory,[10] the Helmholtz free-energy *functional* appears as

$$\mathcal{F}[f(\theta)]=\mathcal{F}_0+\tfrac{1}{2}N\rho\gamma_0+\tfrac{1}{2}N\rho\gamma_2\sigma_2^2+\tfrac{1}{2}N\rho\gamma_4\sigma_4^2+NkT\int f(\theta)\ln f(\theta)\,d\hat{\Omega}, \tag{6}$$

where

$$\gamma_l=\int v_l(r)\,d\vec{r} \tag{7}$$

and

$$\sigma_l=\int f(\theta)P_l(\cos\theta)\,d\hat{\Omega}\,. \tag{8}$$

The last term in Eq. (6) came from expanding the entropy

$$S=-\frac{k}{N!}\int P^{(N)}(1,2,\ldots,N)\times\ln\left(\frac{P^{(N)}(1,2,\ldots,N)}{N!}\right)d\vec{r}_1\,d\hat{\Omega}_1\cdots d\vec{r}_N\,d\hat{\Omega}_N \tag{9}$$

in a cluster series and then truncating the latter by setting $g(1,2)$ and all higher-order correlation functions to unity. The possible phases of the system then emerge from extremizing $\mathfrak{F}[f(\theta)]$ with respect to $f(\theta)$ under the normalization condition

$$\int f(\theta)\,d\hat{\Omega}=1. \tag{10}$$

The resulting equations along with the definition of the order parameters σ_l, Eq. (8), form a self-consistency set:

$$f(\theta)=(1/z)\exp[-B_2P_2(\cos\theta)-B_4P_4(\cos\theta)], \tag{11}$$

with

$$B_2=(\rho\gamma_2/kT)\sigma_2, \tag{12}$$

$$B_4=(\rho\gamma_4/kT)\sigma_4, \tag{13}$$

and

$$z=\int\exp[-B_2P_2(\cos\theta)-B_4P_4(\cos\theta)]\,d\hat{\Omega}. \tag{14}$$

As will be seen later, the same results can be obtained by first differentiating $P^{(1)}$ with respect to θ_1, next introducing into the resulting expression the definition of $P^{(2)}$, and then setting $g(1,2)$ to unity. This alternate derivation makes more explicit the *mean-field* nature of the theory.

Physics resides in the recognition that among the possible phases, the thermodynamical equilibrium phase corresponds to that which minimizes $\mathfrak{F}$. For the equilibrium phase, we thus obtain the free energy $F(\rho,T)$, and from this the equation of state and phase-transition properties.

Such a theory was shown to be rather successful in predicting certain thermodynamic properties of liquid crystals, e.g., phase diagrams for homologous series, order parameters, etc., but very poor in predicting volume changes at transitions, latent heats, and maximum supercooling temperatures. The reason for at least some of its shortcomings is quite clear. Setting $g(1,2)$ to unity ignores all pair correlation effects. While it may be reasonable to apply a mean-field approximation to orientations, omitting all considerations of short-range spatial correlations is too drastic a move, one that is unacceptable at liquid-crystal densities. And yet, a detailed calculation of $g(1,2)$ with a realistic potential is almost unthinkable. We have made such attempts[5,7] for relatively simple potentials, and with the help of simplifying approximations have made some progress in that direction. But our capacity to proceed further is severely strained for want of mathematical skills and computational facilities. Among the disappointments was our inability to calculate the free energy accurately. So, even though all the solutions (representing different possible phases) were at hand, we could not determine which one is statistically stable, and could not obtain $F(\rho,T)$ from which to extract concise, useful information.

On the one hand, then, there is the oversimplification of mean-field theory. On the other hand, there is the intractability of full-fledged statistical mechanics. What we need is something in between. In a recent paper[6] we proposed such a theory, in which pair correlations are accounted for through an orientation-averaged $g(1,2)$. Thus the mean-field approximation is applied only to the orientational part of the problem. As far as spatial correlations are concerened, the system is treated in a manner that recalls the conventional theory of classical liquids. In Ref. 6, the relevant quantities were expressed in terms of "moments" of the potential and were deduced from experimental data. It was a phenomenological theory based on a molecular-theoretic model. For para-azoxyanisole (PAA) and N-(p-methoxybenzylidene)p'-butylaniline (MBBA), the theory gave rise to surprisingly accurate prediction of the volume change, latent heat, and maximum supercooling temperature at isotropic-nematic (I-N) transition. The purpose of the present paper is to strengthen the molecular-theoretic foundation by actually carrying out the appropriate calculations with an assumed potential, in the framework of this "orientation-averaged correlation theory". Since the form of the potential assumed is too simple, we do not expect great things at this stage. Yet, as will be seen, there are moderate successes to encourage continued exploration.

II. ORIENTATION-AVERAGED CORRELATION FUNCTION

The two-particle distribution function, or pair correlation function, $P^{(2)}(1,2)$, is governed by an integro-differential equation which can be derived easily from differentiating the definition of $P^{(2)}(1,2)$ and introducing in the resulting expression the definition of $P^{(3)}(1,2,3)$. We find

$$\nabla_1P^{(2)}(1,2)=P^{(2)}(1,2)\nabla_1\frac{-v(1,2)}{kT}+\int P^{(3)}(1,2,3)\nabla_1\left(\frac{-v(1,3)}{kT}\right)d\vec{r}_3\,d\hat{\Omega}_3. \tag{15}$$

In the isotropic and nematic phases, we can write $P^{(2)}(1,2)$ as in Eq. (5), and

$$P^{(3)}(1,2,3)=\rho^3 f(\theta_1)f(\theta_2)f(\theta_3)\,g^{(3)}(1,2,3)\,. \tag{16}$$

By making the approximations

$$g(1,2)\approx g_e(r_{12})\,, \tag{17}$$

$$g^{(3)}(1,2,3)\approx g_e^{(3)}(r_{12},r_{23},r_{31})\,, \tag{18}$$

we find Eq. (15) readily integrable over the orientations $\hat{\Omega}_1$ and $\hat{\Omega}_2$, yielding

$$\nabla_1 g_e(r_{12})=g_e(r_{12})\nabla_1\left(\frac{-\bar{v}(r_{12})}{kT}\right)+\int g_e^{(3)}(r_{12},r_{23},r_{31})\nabla_1\left(\frac{-\bar{v}(r_{13})}{kT}\right)d\vec{r}_3\,, \tag{19}$$

where

$$\bar{v}(r_{12})=v_0(r_{12})+v_2(r_{12})\sigma_2^2+v_4(r_{12})\sigma_4^2\,. \tag{20}$$

Equation (19) is in the familiar form known as the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) equation in the theory of classical liquids. Given a reasonably approximated $g_e^{(3)}(r_{12},r_{23},r_{31})$, such as the Kirkwood superposition approximation,

$$g_e^{(3)}(r_{12},r_{23},r_{31})\approx g_e(r_{12})g_e(r_{23})g_e(r_{31})\,, \tag{21}$$

this highly nonlinear equation can be solved numerically using as input the effective potential $\bar{v}(r)$. Note that $\bar{v}(r)$, and thus $g_e(r)$, depends on the order parameters. This dependence is responsible for a second fold of self-consistency, as will be seen.

$g_e(r)$ is what we shall refer to as the "orientation-averaged correlation function". Physically, it can be looked at as the spatial correlation function between two rapidly rotating molecules, their interaction resulting from averaging Eq. (1) with the one-particle distribution functions $f(\theta_1)$ and $f(\theta_2)$ serving as weights.

To study the consequence of introducing such a correlation function, let us derive the equation that governs $P^{(1)}(1)$. Differentiating the definition of $P^{(1)}(1)$ with respect to θ_1 leads to

$$\frac{d}{d\theta_1}\ln f(\theta_1)=\frac{-\rho}{kT}\int f(\theta_2)g(1,2)\times\frac{\partial}{\partial\theta_1}[v_2(r_{12})P_2(\hat{\Omega}_1\cdot\hat{\Omega}_2)+v_4(r_{12})P_4(\hat{\Omega}_1\cdot\hat{\Omega}_2)]\,d\vec{r}_2\,d\hat{\Omega}_2\,. \tag{22}$$

In the zeroth-order approximation, $g(1,2)$ is set to unity. The differentiation on the right-hand side can be taken outside the integral. By integrating over θ_1, we reproduce Eqs. (11)–(14), the Maier-Saupe theory. But here, in this more sophisticated theory, we wish to substitute $g_e(r_{12})$ for $g(1,2)$. As a consequence we obtain

$$f(\theta)=\frac{1}{z(\sigma^2)}\exp\left(\frac{-\rho\sigma_2}{kT}\gamma_2(\sigma^2)P_2(\cos\theta)-\frac{\rho\sigma_4}{kT}\gamma_4(\sigma^2)P_4(\cos\theta)\right), \tag{23}$$

with

$$\gamma_l(\sigma^2)=\int v_l(r)g_e(r\,|\,\sigma^2)\,d\vec{r}\,. \tag{24}$$

In fact, Eq. (23) is identical to Eqs. (11)–(13) except that γ_l now depends on the order parameters through $g_e(r)$. We have explicitly displayed the order-parameter dependence of g_e, γ_l, and z, as shown, as a reminder to the reader. Actually there are even more complications: Since $g_e(r)$ depends on the thermodynamic environment [see Eq. (19)], all these quantities vary with ρ and T as well, both indirectly through $g_e(r)$, and even more indirectly through $\sigma(\rho, T)$. Equations (8), (23), and (24) provide the first fold of self-consistency.

The program now goes as follows. Given ρ and T, one starts with some initial values of σ_2 and σ_4, e.g., those from the Maier-Saupe theory. One calculates from Eq. (20) the effective pair potential $\bar{v}(r)$, and solves Eq. (19) for $g_e(r\,|\,\sigma^2)$. The results are then used in Eq. (24) for γ_l. Equations (8) and (23) are next solved self-consistently. The resulting σ_2 and σ_4 will in general differ from their initial values. An iterative process will thus be needed to achieve the second fold of self-consistency. [In practice it is more efficient to solve the BBGKY equation (19) for a set of σ_2 and σ_4, and subsequently deal with Eqs. (8) and (23) graphically.]

III. FREE ENERGY

A natural extension of the mean-field theory would call for the inclusion of a second entropy term in the free-energy functional, Eq. (6). Cluster expanding Eq. (9) and using the $g_e(r)$ approximation, one finds

$$S=S_{\text{ideal}}-Nk\ln\rho+k\ln N!-Nk\int f(\theta)\ln f(\theta)\,d\hat{\Omega}-\tfrac{1}{2}N\rho k\int g_e(r)\ln g_e(r)\,d\vec{r}+\cdots\,. \tag{25}$$

Thus

$$\mathfrak{F}=\mathfrak{F}_0+\tfrac{1}{2}N\rho\gamma_0+\tfrac{1}{2}N\rho\gamma_2\sigma_2^2+\tfrac{1}{2}N\rho\gamma_4\sigma_4^2+NkT\int f(\theta)\ln f(\theta)\,d\hat{\Omega}+\tfrac{1}{2}N\rho kT\int g_e(r)\ln g_e(r)\,d\vec{r}+\cdots\,. \tag{26}$$

Unfortunately, this expression is not reliable since there is no way to guarantee that the expansion will converge, let alone do so in just two terms. Offhand one might see a glimpse of hope: what one needs is not so much the free energy, but the free-energy *difference* between the isotropic and nematic phase, i.e., between the free energies at zero and finite-order parameter values. This difference can be written as

$$\begin{aligned}\Delta\mathfrak{F} = {} & \tfrac{1}{2}N\rho[\gamma_0(\sigma^2)-\gamma_0(0)]+\tfrac{1}{2}N\rho\gamma_2(\sigma^2)\sigma_2^2 \\ & +\tfrac{1}{2}N\rho\gamma_4(\sigma^2)\sigma_4^2+NkT \\ & \times\left[\int f(\theta)\ln f(\theta)\,d\hat{\Omega}-\ln\frac{1}{4\pi}\right] \\ & +\tfrac{1}{2}N\rho kT\left[\int g_e(r\,|\sigma^2)\ln g_e(r\,|\sigma^2)\,d\vec{\mathrm{r}}\right. \\ & \left.-\int g_e(r\,|0)\ln g_e(r\,|0)\,d\vec{\mathrm{r}}\right]+\cdots\,. \end{aligned} \tag{27}$$

The terms within square brackets measure the lowering of free energy as orientational ordering takes place. And since the latter is regarded as weak enough to permit a mean-field approximation, one is led to believe that multiparticle cluster terms such as the last term in Eq. (27) should decrease rapidly. A more careful look at the expansion, however, reveals that one still faces a density expansion, which is not expected to converge well at liquid-crystal densities. Equation (26) is therefore not trustworthy.

We propose here a new method to obtain the free-energy functional, one which is free of expansions. For clarity, let us do it without $v_4(r)$, and thus without γ_4 and σ_4. Write

$$\begin{aligned}\mathfrak{F}[f(\theta)] = {} & \mathfrak{F}_0+NkT\left[\int f(\theta)\ln f(\theta)\,d\hat{\Omega}-\ln\left(\frac{1}{4\pi}\right)\right] \\ & +\tfrac{1}{2}N\rho\lambda(\sigma_2^2)\,, \end{aligned} \tag{28}$$

where $\lambda(\sigma_2^2)$ is as yet an unknown function. Varying $\mathfrak{F}$ with respect to $f(\theta)$ under the normalization condition (10) leads to a Euler-Lagrange equation whose solution is

$$\ln f(\theta)=\frac{-\rho\sigma_2}{kT}\left(\frac{d\lambda(\sigma_2^2)}{d\sigma_2^2}\right)P_2(\cos\theta)-\ln z(\sigma_2^2)$$

or

$$f(\theta)=\frac{1}{z(\sigma_2^2)}\exp\left[\frac{-\rho\sigma_2}{kT}\left(\frac{d\lambda(\sigma_2^2)}{d\sigma_2^2}\right)P_2(\cos\theta)\right]\,. \tag{29}$$

Comparing this with Eq. (23) with the γ_4 term omitted, we find

$$d\lambda(\sigma_2^2)/d\sigma_2^2=\gamma_2(\sigma_2^2)\,, \tag{30}$$

or, by integration,

$$\lambda(\sigma_2^2)=\lambda(0)+\int_0^{\sigma_2^2}\gamma_2(x)\,dx\,. \tag{31}$$

Since $\gamma_2(x)$ has been well defined by Eq. (24), we have $\lambda(\sigma_2^2)$ and the free-energy expression.

At the center of this derivation is the assumption that Eq. (23) is accurate. While our new free-energy expression is certainly not universally valid, it is totally consistent with our orientation-averaged correlation approximation. This is as much as we wish to claim, and as much as we need in our theory.

IV. NUMERICAL APPLICATION TO PAA

To illustrate the application of our theory, we chose a simple potential to mimic para-azoxyanisole (PAA). We took

$$\begin{aligned} & v_0(r)=4\epsilon_0[(a_0/r)^{12}-(a_0/r)^6]\,, \\ & v_2(r)=-4\epsilon_2(a_2/r)^6\,, \\ & v_4(r)=0\,, \end{aligned} \tag{32}$$

with

$$\epsilon_0=145.426\;k\,{}^\circ\mathrm{K}\,,$$

$$\epsilon_2=96.950\;k\,{}^\circ\mathrm{K}\,,$$

and

$$a_0=a_2=6.348\,823\;\mathrm{\mathring{A}}\,,$$

so as to fix the isotropic-nematic transition at approximately 408 °K when the specific volume $v = 374.94\ \mathrm{\mathring{A}}^3$ (or density $\rho=0.002\,667\ \mathrm{\mathring{A}}^{-3}$), the experimental values.

Calculations were carried out at densities ranging from $0.002\,667\ \mathrm{\mathring{A}}^{-3}$ to $0.002\,674\ \mathrm{\mathring{A}}^{-3}$ and temperatures ranging from 404 °K to 408 °K. At every choice of (ρ, T), a range of σ_2—usually between 0 and 0.52—were used to calculate $\overline{v}(r\,|\,\sigma^2)$ and solve the BBGKY equation (19) for $g_e(r\,|\sigma^2)$. Among the output were the corresponding values of $\gamma_0(\sigma_2^2)$ and $\gamma_2(\sigma_2^2)$, as obtained from the defining equation (24). Equation (23) then gave us $f(\theta)$; from which and from Eq. (8) we obtained the outcoming σ_2's. Obviously, the outcoming and ingoing σ_2's did not agree except at the one σ_2 which represents the double self-consistency solution. The latter we found graphically. It was necessary to pinpoint the σ_2 solution to, say, three decimal places, which was time-consuming work. However, since $\gamma_2(\sigma_2^2)$ turned out rather flat, relatively wide intervales in σ_2 (e.g., 0.05) would suffice for use in the integral of Eq. (31). This greatly reduced computational demands. Table I shows a typical set of results obtained.

The next step concerned free-energy calculations

TABLE I. Self-consistent solution at $\rho = 0.002\,667$ Å^{-3} and $T = 407$ °K.

Input	Output			
σ_2	σ_2	$-\gamma_2$(°KÅ^3)	$-\rho_2\gamma_2/kT$	σ_4
0.00	0.000 000	678 993	4.449 32	0.0000
0.05	0.045 853	679 210	4.450 75	0.0015
0.10	0.094 167	679 871	4.455 08	0.0061
0.15	0.144 458	680 984	4.462 37	0.0141
0.20	0.196 134	682 565	4.472 73	0.0256
0.25	0.248 521	684 646	4.486 37	0.0406
0.30	0.300 894	687 242	4.503 38	0.0591
0.35	0.352 541	690 411	4.524 14	0.0809
0.40	0.402 799	694 219	4.549 09	0.1055
0.45	0.451 103	698 766	4.578 89	0.1328
0.46	0.460 538	699 861	4.586 07	0.1385
0.468	0.467 977	700 698	4.591 55	0.1431
0.47	0.469 826	700 910	4.592 94	0.1443
0.48	0.479 014	701 997	4.600 07	0.1502
0.49	0.488 099	703 125	4.607 46	0.1561

at the solutions. Equations (28) and (31) were used. At each density ρ, then, by evaluating the free-energy difference

$$F_N - F_I \equiv \mathfrak{F}[f_N(\theta)] - \mathfrak{F}[f_I(\theta)] \equiv \mathfrak{F}[\sigma_2] - \mathfrak{F}[0]$$
$$= NkT\left[\int f_N(\theta)\ln f_N(\theta)\,d\hat{\Omega} - \ln\left(\frac{1}{4\pi}\right)\right]$$
$$+ \tfrac{1}{2}N\rho[\lambda(\sigma_2^2) - \lambda(0)]\,, \tag{33}$$

we were able to identify the *constant-volume* transition temperature $T_{IN}(\rho)$, which is lower than the true transition temperature (at constant pressure) T_{IN} by about 3 °K. (see the analysis in Ref. 6). Table II lists some of the information obtained. The constant-volume transition temperatures are identified in the table.

Assuming that conclusions drawn from constant-volume transitions are not too distorted from those based on the true transitions, we read from Table II three immediate consequences of the calculation. First, the order-parameter jump is 0.495, which is quite far from the Maier-Saupe value of 0.43. That it differs significantly from the experimental value[11–14] of 0.35–0.40 does not worry us. It stands at about 0.46 at 407–408 °K. By adjusting $v_4(r)$, one could always lower it to fit the experiment. Clearly it will no longer be universal in our theory. Second, the order-parameter jump remains constant along the transition curve. This is consistent with experimental finding,[11] and is most encouraging. That the Maier-Saupe theory yields such a result is not surprising since it gives rise to a *universal* phase diagram and a *universal* order-parameter jump. But such a result was not *a priori expected* to hold in our theory. Third, even though the $\ln T_{IN}(\rho)$-$\ln v$ plot gives us a straight line, the slope of 1.45 is quite far from the experimental value[11] of 4.0. This indicates that short-range order must yet be considered more carefully. Our feeling is that it is not the orientation-averaging that is at fault, but that *anisotropic* steric effect leaves a more important imprint on the quantity $\Gamma \equiv -[d\ln T_{IN}(\rho)/d\ln v]$ than on other thermodynamic properties. We intend to study the effect of incorporating into our theory potential terms that depend on $\hat{\Omega}_1\cdot\hat{r}_{12}$ and $\hat{\Omega}_2\cdot\hat{r}_{12}$, which were found earlier[2] to mimic anisotropic repulsions.

The numerical results can be used to deduce a number of other properties. First, the temperature dependence of the order parameter. Figure 1 reproduces experimental data by Pines *et al.*,[13]

TABLE II. Free energy calculations at selected densities and temperatures.

			Free-energy difference (°K/Nk)		
ρ(Å^{-3})	T(°K)	σ_2	$Nk[\int f_N(\theta)\ln f_N(\theta)d\hat{\Omega} - \ln(1/4\pi)]$	$\frac{1}{2}N\rho[\lambda(\sigma_2^2) - \lambda(0)]$	$F_N - F_I$
0.002 667	408	0.452	189.39	−187.64	1.75
	407	0.468	202.57	−201.34	1.23
	406	0.480	212.69	−211.95	0.74
	405	0.490	221.28	−221.00	0.28
T_{IN}	404.45	0.495			0
	404	0.500	230.03	−230.26	−0.23
0.002 670	407	0.475	208.75	−207.81	0.94
	406	0.486	218.13	−217.69	0.44
T_{IN}	405.11	0.495			0
	405	0.496	226.82	−226.88	−0.06
	404	0.505	234.75	−235.32	−0.57
0.002 674	407	0.4835	216.40	−215.85	0.55
	406	0.4938	225.32	−225.28	0.04
T_{IN}	405.92	0.495			0
	405	0.5035	233.84	−234.36	−0.52

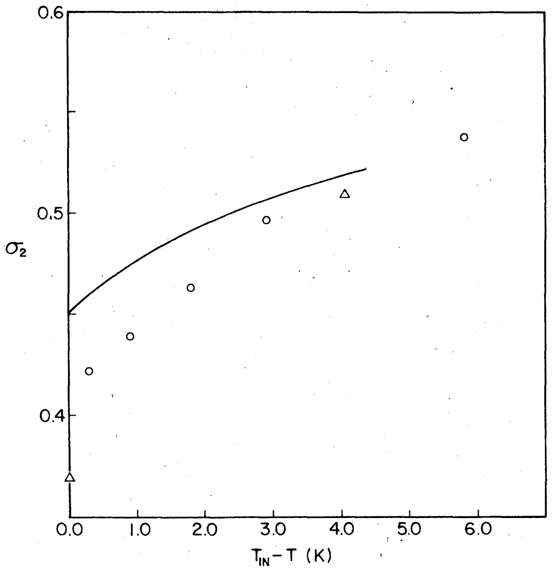

FIG. 1. $\sigma_2(T)$ at 1 atm. ○, Pines *et al.* (Ref. 13); △, Hanson and Shen (Ref. 14); curve, theory.

and Hanson and Shen.[14] There are several points to ponder before a comparison of our results to the data can be made. (i) Without the aid of a $v_4(r)$ term, our order parameter at transition is quite a bit higher than the experimental value. There is no rational way to "normalize" our results to fit the experiment. (ii) While our constant-volume transition temperature $T_{IN}(\rho)$ can be located accurately, the determination of the *true* transition temperature is somewhat model dependent. By identifying $T_{IN}(\rho)$ with the maximum supercooling temperature as in Ref. 6, we locate the true transition temperature at 407.5 °K. In Fig. 1 it will be taken as 408 °K for convenience. (iii) The data are at constant pressure. We must therefore first obtain at various temperatures densities which correspond to the same pressure, and then plot the order parameters obtained at those (ρ, T) pairs. Table III gives a list of (ρ, T), at $P=1$ atm, as interpolated from the Maier-Saupe data[10] and scaled to give $\rho = 0.002\,667$ Å^{-3} at $T=408$ °K. The curve shown in Fig. 1 resulted from our analysis. In view of the points mentioned above, a real quantitative comparison with data is not meaningful. We are, however, encouraged by the qualitative consistency between our results and experiment.

TABLE III. Density vs temperature[10] at $P=1$ atm (normalized to $\rho = 0.000\,266\,7$ Å^{-3} at $T=408$ °K and used for computing $\sigma_2(T)$ in Fig. 1.)

T (°K)	$T_{IN}-T$ (°K)	v (Å^3)	ρ (Å^{-3})
408	0.0	374.95	0.002 667 0
407	1.0	374.42	0.002 670 8
406	2.0	373.97	0.002 674 0
405	3.0	373.59	0.002 676 7
404	4.0	373.19	0.002 679 6

We have not compared our $\sigma_2(T)$ at constant volume to the data of Ref. 11 since the latter at $v=221$ cm^3/mole $= 366.80$ Å^3 lies far outside the range of densities considered by us. Sketching our results alongside those of Ref. 11 indicates that our temperature dependence may be quite a bit stronger, but this is inconclusive.

The calculation of $\sigma_2(T)$ at constant pressure offers a useful check on the value Γ. Let v_1 and v_2 denote the specific volumes at T_1 and T_2, respectively, at $P=1$ atm. Then, provided that $v_1 \approx v_2$, we have

$$\sigma_2(v_2, T) \approx \sigma_2(v_1, T) + \left(\frac{\partial \sigma_2(v, T)}{\partial v}\right)_{v_1}(v_2 - v_1)\,. \tag{34}$$

But since

$$\begin{aligned}\frac{\partial \sigma_2(v,T)}{\partial v} \equiv \left(\frac{\partial \sigma_2}{\partial v}\right)_T &= -\left(\frac{\partial T}{\partial v}\right)_{\sigma_2}\left(\frac{\partial \sigma_2}{\partial T}\right)_v \\ &= -\left(\frac{\partial \ln T}{\partial \ln v}\right)_{\sigma_2}\left(\frac{T}{V}\right)\left(\frac{\partial \sigma_2}{\partial T}\right)_v ,\end{aligned} \tag{35}$$

and

$$-\left(\frac{\partial \ln T}{\partial \ln v}\right)_{\sigma_2} = \left(\frac{\partial \ln T}{\partial \ln \rho}\right)_{\sigma_2} \approx \Gamma\,, \tag{36}$$

as was observed earlier, Eq. (34) becomes

$$\sigma_2(v_2, T) \approx \sigma_2(v_1, T) + \Gamma T\left(\frac{\partial \sigma_2}{\partial T}\right)_{v_1}\left(\frac{v_2}{v_1} - 1\right),$$

or

$$\Gamma \approx [\sigma_2(v_2, T) - \sigma_2(v_1, T)]\left[T\left(\frac{\partial \sigma_2}{\partial T}\right)_{v_1}\left(\frac{v_2}{v_1} - 1\right)\right]^{-1}. \tag{37}$$

The Γ value thus obtained from our results turned out to be about 1.3, within numerical uncertainty from the directly obtained value of 1.45. This merely serves as a consistency check since our Γ differs significantly from the experimental value of 4.0.

Next, using the theoretical results listed in Table II, we were able to calculate the volume change at transition $\Delta v/v$ and the latent heat ΔH. The knowledge of $F_N - F_I$ at a range of (ρ, T) gave us the pressure change and the entropy change at fixed *volume v*. In the notations of Fig. 2, the pressure change was given by

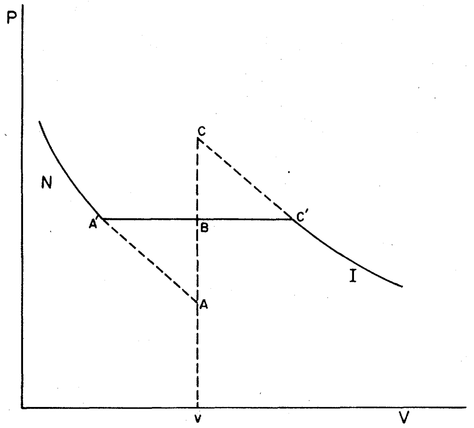

FIG. 2. Graphic aid for carrying out a Maxwell construction.

$$P_C - P_A \equiv P_I(\rho, T) - P_N(\rho, T)$$

$$= -\left(\frac{\partial(F_I - F_N)}{\partial v}\right)_{\rho, T} = 0.69\ {}^\circ\mathrm{K}\,\mathrm{\AA}^{-3} \qquad (38)$$

at $\rho = 0.002\,667\ \mathrm{\AA}^{-3}$ and $T = 407.5\ {}^\circ\mathrm{K}$. The entropy change was given by

$$S_C - S_A = S_I(\rho, T) - S_N(\rho, T)$$

$$= -\left(\frac{\partial(F_N - F_I)}{\partial T}\right)_{\rho, T} = 0.52\,k\,. \qquad (39)$$

From thermodynamics, a Maxwell construction led to

$$\Delta v / v \approx K(P_C - P_A) = 0.714\%\,, \qquad (40)$$

where K denotes the isothermal compressibility, and was taken to be $7.5 \times 10^{-11}\ \mathrm{cm}^2/\mathrm{dyne}$ from Ref. 6, based on Ref. 15. Also,

$$\Delta H = T[(S_{C'} - S_C) - (S_{A'} - S_A)] + T(S_C - S_A)$$

$$\approx (\beta T/\kappa)\Delta v + T(S_C - S_A) = 2448\ \mathrm{J/mole}, \qquad (41)$$

where β denotes the coefficient of thermal expansion and was taken to be $7.8 \times 10^{-4}\ {}^\circ\mathrm{K}^{-1}$ from Ref. 14. The second line of Eq. (41) came from the realization that

$$(S_{C'} - S_C) - (S_{A'} - S_A) \approx (v_{C'} - v_C)\left(\frac{\partial S}{\partial v}\right)_{T|C'} - (v_{A'} - v_A)\left(\frac{\partial S}{\partial v}\right)_{T|A'}$$

$$\approx \tfrac{1}{2}\Delta v\left[\left(\frac{\partial S}{\partial v}\right)_{T|C'} + \left(\frac{\partial S}{\partial v}\right)_{T|A'}\right],$$

$$\left(\frac{\partial S}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v = \frac{\beta}{\kappa}$$

and

$$\beta_{C'} \approx \beta_{A'}\,.$$

Experimental data[12] gave $\Delta v/v = 0.30\%–0.36\%$ and $\Delta H = 574–760$ J/mole, so our results are too big by a factor of 2–4. We are not surprised by this discrepancy. With the knowledge that γ_2 varies slowly with σ_2^2, a little analytical work on the separate terms in Eq. (28) convinces us that $(F_N - F_I)$ varies roughly as σ_2^2. The numbers in Table II lend further support: all separate contributions to $F_N - F_I$ vary as σ_2^2 to well within 1% for all cases considered. Since our σ_2^2 at transition is significantly larger than the experimental value $F_N - F_I$ and thus all quantities which are proportional to $F_N - F_I$, e.g., $\Delta v/v$ and ΔH, would be too big by the same ratio, which accounts for a factor of 2.

A final note on the dependence of γ_2 on ρ and T. We found

$$\gamma_2 \propto \rho^{1.11} T^{-0.95}\,, \qquad (42)$$

in total contrast to our expectation[6] of a nearly linear temperature dependence, which gave rise to good theoretical values of phase-transition properties when used in a phenomenological analysis.[6] This suggests that our model potential is much too unrealistic. More work is required along the present direction to establish a sound molecular model for liquid crystals.

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