Anisotropic steric effects and negative $\langle P_4 \rangle$ in nematic liquid crystals

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Starting with a model intermolecular potential that includes $\hat{\Omega} \cdot \hat{r}$ terms to account for anisotropic steric interactions, we carry out a statistical mechanical calculation in the cell approximation, and apply it specifically to the isotropic-nematic transition of methoxybenzylidene butylaniline (MBBA). The potential is determined to fit the experimental transition temperature T_{IN} and the discontinuity in the orientational order parameter $\langle P_2 \rangle$ at transition. $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are then calculated from solving a set of coupled self-consistency equations for the orientational and spatial parts of the distribution function, as are other phase-transition properties. There are improvements over model calculations which do not account for anisotropic steric effects, but the improvements are generally less than significant. The most striking result is that a *stable* nematic phase *requires* $\langle P_4 \rangle$ to be negative at and near the transition. It is a theoretical result qualitatively consistent with experimental data but has not been attained until now.

I. INTRODUCTION

The theory of liquid crystals has been developing in two major directions. One, the Landau—de Gennes theory,[1] employs a phenomenological approach. The Helmholtz free energy is expanded in powers of the order parameter and its gradient, requiring in the process five or more material parameters to be determined by experimental data. The theory contains a simple temperature dependence and no volume dependence. In the treatment of pretransitional effects, terms of higher order than quadratic are usually omitted. Such a theory is physically appealing, mathematically convenient, and qualitatively powerful. Quantitatively, however, it encounters difficulties that result from oversimplification.[2]

The other approach is the "molecular" theory, defined as one that begins with a model, be it in the form of rods or interparticle potentials. Conventional statistical methods are applied to obtain distribution functions, free energies, thermodynamic and phase-transition properties, and dynamical correlations.[3] The major difficulty in this approach is that model construction and statistical calculation need be carried out simultaneously; both the mathematical derivation and the numerical computation can be overwhelmingly demanding. As a consequence, too many simplifying approximations are made—in the choice of models, in statistical mechanical approximation schemes, and in the evaluation of thermodynamic quantities. We shall come back to each of these issues presently, in Sec. II.

In our group we have devoted a large part of our effects on liquid crystals to the molecular theoretical approach. Using relatively simple models first suggested by Kobayashi and McMillan[4]—models without anisotropic steric effects—we have obtained reasonably good, semi-

quantitative agreement with experiment in several cases,[5] as have other authors.[3] But there remain puzzling discrepancies, some of which have resulted in a certain degree of unease toward the usefulness of molecular theories. We cite here the following as examples.

(i) The calculated temperature dependence of the orientational order parameter $\sigma_2 \equiv \langle P_2 \rangle$ (and $\sigma_4 \equiv \langle P_4 \rangle$) is too weak.

(ii) σ_4 itself, calculated at or near the isotropic-nematic transition temperature T_{IN}, is too large. In particular, calculations for *stable* nematic phases always yield positive σ_4, while experiment on certain nematic substances [e.g., methoxybenzylidene butylaniline (MBBA)] gives rise to negative σ_4 near T_{IN}.

(iii) The derivative $d \ln T_{IN}(\rho)/d \ln \rho$, or $d \ln T(\rho)/d \ln \rho$ at constant σ_2, is always too small, by a factor of 3 to 4.

(iv) The calculated latent heat at *I-N* transition is usually too large, by a factor of about 2 to 3.

II. MODEL AND FORMALISM

A. Model

We use a potential model. The interaction between a pair of cylindrically symmetrical nonchiral molecules is described as

$$v(i,j) = v(r_{ij}, \hat{\Omega}_i \cdot \hat{\Omega}_j, \hat{\Omega}_i \cdot \hat{r}_{ij}, \hat{\Omega}_j \cdot \hat{r}_{ij})$$

$$\approx v_0(r_{ij}) + v_2(r_{ij}) P_2(\hat{\Omega}_i \cdot \hat{\Omega}_j) + v_4(r_{ij}) P_4(\hat{\Omega}_i \cdot \hat{\Omega}_j)$$

$$+ w_2(r_{ij})[P_2(\hat{\Omega}_i \cdot \hat{r}_{ij}) + P_2(\hat{\Omega}_j \cdot \hat{r}_{ij})] , \qquad (1)$$

where $\vec{r}_i$ and $\hat{\Omega}_i$ denote the position of the center of mass of the ith molecule and its orientation, respectively. The first three terms represent the popular McMillan form of the potential,[4,5] and the last term, which couples spatial

and orientational variables, stands for the leading anisotropic steric correction. In an earlier paper we inspected the effect of a weak anisotropy by treating $w_2(r)$ as a perturbation. The results obtained were not particularly informative.[6] From fitting potential profiles obtained from Eq. (1) to those obtained with rod models, we learned that $w_2(r)$ should be rather large compared to $v_2(r)$ and $v_4(r)$ even for rods which are short and relatively soft.[7] Thus, there is no way to avoid treating $w_2(r)$ on an equal basis as $v_2(r)$ and $v_4(r)$ in a full-fledged statistical calculation.

In this work we shall parametrize the potentials as follows:

$$v_l(r) = a_l \exp(-\beta^2 r^2) , \quad l = 0, 2, 4$$
$$w_2(r) = b_2 \exp(-\beta^2 r^2) . \tag{2}$$

The potential parameters are a_0, a_2, a_4, b_2, and β.

B. Statistical formalism

Conventional statistical treatment of a classical system of N particles in a volume V ($\rho \equiv N/V$), at temperature T, begins with the Boltzmann distribution

$$P_N^0(1, 2, \ldots, N) = \frac{N!}{Z} \exp\left[-\sum_{i<j} \frac{v(i,j)}{kT} \right] , \tag{3}$$

where Z denotes the partition function

$$Z = \int \exp\left[-\sum_{i<j} \frac{v(i,j)}{kT} \right] d1\,d2 \cdots dN , \tag{4}$$

$di \equiv d\vec{r}_i d\hat{\Omega}_i$, and $N!$ is an (arbitrary) normalization factor. The one-particle distribution function

$$P_1^0(1) \equiv \rho f(\vec{r}_1, \hat{\Omega}_1) = \frac{N}{Z} \int \exp\left[-\sum_{i<j} \frac{v(i,j)}{kT} \right] d2 \cdots dN , \tag{5}$$

is also the density function, which contains information on macroscopic long-range order in the system. $P_1^0(1)$, or $f(\vec{r}, \hat{\Omega})$, is the weighting function used for evaluating the order parameter $\langle P_l \rangle$. The two-particle distribution function

$$P_2^0(1,2) \equiv P_1^0(1)P_1^0(2)g(1,2)$$
$$= \frac{N(N-1)}{Z} \int \exp\left[-\sum_{i<j} \frac{v(i,j)}{kT} \right] d3 \cdots dN , \tag{6}$$

gives a measure of the short-range pairwise correlation between the molecules. $P_1^0(1)$ and $P_2^0(1,2)$ can, at least in principle, be calculated by means of cluster-expansion procedures, integral equations, molecular dynamics, or Monte Carlo methods.

The Helmholtz free energy of a system can be expressed as

$$F = F_0 + \int \sum_{i<j} v(i,j) \frac{P_N^0(1,2,\ldots,N)}{N!} d1 \cdots dN$$
$$+ kT \int \frac{P_N^0(1,2,\ldots,N)}{N!}$$
$$\times \ln \frac{P_N^0(1,2,\ldots,N)}{N!} d1 \cdots dN . \tag{7}$$

F_0 is the ideal-gas term. The potential energy, i.e., the second term, can be reduced in one step to an integral over $v(i,j)P_2^0(i,j)$. The last term, from entropy, however, cannot be reduced to a closed form involving low order $P_n^0(1,\ldots,n)$. It can be expanded in a cluster series, but one that does not converge rapidly when the system is at liquid densities.

We introduced in Ref. 8 a variational approach which turns out to be most convenient for treating phase transitions associated with nonspatial degrees of freedom. It begins with considering the undetermined N-particle distribution function $P_N(1,2,\ldots,N)$ and a free-energy functional

$$\mathcal{F}\{P_N\} = F_0 + \int \sum_{i<j} v(i,j) \frac{P_N(1,2,\ldots,N)}{N!} d1 \cdots dN$$
$$+ kT \int \frac{P_N(1,2,\ldots,N)}{N!}$$
$$\times \ln \frac{P_N(1,2,\ldots,N)}{N!} d1 \cdots dN . \tag{8}$$

Minimization of the latter under the constraint

$$\int P_N(1,2,\ldots,N) d1 \cdots dN = N! , \tag{9}$$

yields immediately the Boltzmann distribution, Eq. (3). This permits us to "model" $P_N(1,2,\ldots,N)$ in various stages of approximation. For example, writing $P_N(1,2,\ldots,N)$ as $N! \prod_{i=1}^{N} Q(\hat{\Omega}_i)$, and then minimizing $\mathcal{F}$ with respect to $Q(\hat{\Omega})$, leads immediately to the Maier-Saupe mean-field approximation. Writing $P_N(1,2,\ldots,N)$ as

$$N! \left[\prod_{i=1}^{N} Q(\hat{\Omega}_i) \right] \Phi(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) ,$$

and then minimizing $\mathcal{F}$ with respect to Q and Φ, gives rise to[6] a formalism in which the orienting forces are modified by pair distribution functions, which are in turn solved for orientationally averaged intermolecular forces. Such an approximate treatment of space-orientation coupling was named the "orientationally averaged pair correlations" theory (OAPC).[5,8]

The optimized $P_N(1,2,\ldots,N)$, when substituted back into $\mathcal{F}\{P_N\}$, gives us a Helmholtz free energy which is *exact for that level of approximation*, without the need of a seriously questionable cluster-expansion procedure.

C. Cell approximation

Spatial correlations play an important role in the theory of high-density fluids. For liquid crystals, one way to take them into account is to borrow from the theory of classical liquids, as in Refs. 5, 6, and 8. The other is to use a cell approximation: Use a single-particle approximation and restrict the motion of molecules to individual cells. The fluidity manifests itself through large excursions of molecules from the centers of their cells. In this paper we adopt the latter method for the sake of computational economy. The model for $P_N(1,2,\ldots,N)$ is then given by

$$P_N(1,2,\ldots,N)=N!\prod_{i=1}^{N}[Q(\hat{\Omega}_i)\phi(\vec{r}_i-\vec{R}_i)] , \qquad (10)$$

where $\{\vec{R}_i\}$ represent lattice points about which the cells are centered.

Using Eq. (10) in Eq. (8), we find

$$\mathcal{F}\{Q,\phi\}=F_0+\sum_{i<j}\int v(i,j)Q(\hat{\Omega}_i)Q(\hat{\Omega}_j)\prod_k\phi(\vec{r}_k-\vec{R}_k)d\hat{\Omega}_id\hat{\Omega}_jd\vec{r}_1\cdots d\vec{r}_N$$

$$+kT\sum_i\int Q(\hat{\Omega}_i)\ln Q(\hat{\Omega}_i)d\hat{\Omega}_i+kT\int\prod_m\phi(\vec{r}_m-\vec{R}_m)\ln\prod_k\phi(\vec{r}_k-\vec{R}_k)d\vec{r}_1\cdots d\vec{r}_N$$

$$=F_0+\frac{1}{2}\sum_{i<j}\int\bar{v}(i,j)\phi(\vec{r}_i-\vec{R}_i)\phi(\vec{r}_j-\vec{R}_j)d\vec{r}_id\vec{r}_j$$

$$+kT\sum_i\int Q(\hat{\Omega}_i)\ln Q(\hat{\Omega}_i)d\hat{\Omega}_i+kT\sum_k\int\phi(\vec{r}_k-\vec{R}_k)\ln\phi(\vec{r}_k-\vec{R}_k)d\vec{r}_k , \qquad (11)$$

with

$$\bar{v}(i,j)=\int v(i,j)Q(\hat{\Omega}_i)Q(\hat{\Omega}_j)d\hat{\Omega}_id\hat{\Omega}_j , \qquad (12)$$

an orientationally averaged pairwise potential.

Before embarking upon a variational treatment of $\mathcal{F}\{Q,\phi\}$, let us require that $Q(\hat{\Omega})$ be dependent only on $\hat{\Omega}\cdot\hat{n}$, where $\hat{n}$ denotes the director. This requirement is consistent with the uniaxial property of nematics. On the other hand, it is not obvious that the solutions of the variational equations are necessarily uniaxial. We shall return to this point later and in the Appendix.

We now vary $\mathcal{F}\{Q,\phi\}$ with respect to $Q(\hat{\Omega})$ and $\phi(\vec{r}-\vec{R})$ under the normalization constraints

$$\int Q(\hat{\Omega})d\hat{\Omega}=1 \qquad (13)$$

and

$$\int\phi(\vec{r}-\vec{R})d\vec{r}=1 . \qquad (14)$$

The Euler-Lagrange equation for $\phi(\vec{r}-\vec{R})$ gives rise to the following solution:

$$\phi(r-R)=\frac{1}{Z_\phi}e^{-V(\vec{r}-\vec{R})/kT} , \qquad (15)$$

with

$$V(\vec{r}_1-\vec{R}_1)=\sum_{k\neq1}\int\bar{v}(k,1)\phi(\vec{r}_k-\vec{R}_k)d\vec{r}_k , \qquad (16)$$

and

$$Z_\phi=\int e^{-V(\vec{r}-\vec{R})/kT}d\vec{r} . \qquad (17)$$

$V(\vec{r}_1-\vec{R}_1)$ is clearly seen as a mean field experienced by molecule 1, obtained by first averaging $v(k,1)$ over all orientations of molecules k and 1, then over all possible positions of molecule k in its cell, and finally summed over all cells except the one occupied by molecule 1.

The Euler-Lagrange equation for $Q(\hat{\Omega})$ under the assumption that $Q(\hat{\Omega})=Q(\hat{\Omega}\cdot\hat{n})$ yields

$$Q(\hat{\Omega})=\frac{1}{Z_Q}\exp\left[-\frac{1}{kT}[(G_2\sigma_2+K_2)P_2(\hat{\Omega}\cdot\hat{n})\right.$$

$$\left.+G_4\sigma_4P_4(\hat{\Omega}\cdot\hat{n})]\right] , \qquad (18)$$

where

$$\sigma_l=\int Q(\hat{\Omega})P_l(\hat{\Omega}\cdot\hat{n})d\hat{\Omega} , \quad l=2,4 \qquad (19)$$

$$Z_Q=\int\exp\left[-\frac{1}{kT}[(G_2\sigma_2+K_2)P_2(\hat{\Omega}_1\cdot\hat{n})\right.$$

$$\left.+G_4\sigma_4P_4(\hat{\Omega}_1\cdot\hat{n})]\right]d\Omega_1 , \qquad (20)$$

$$G_l=\sum_{k\neq1}\gamma_l(\vec{R}_k,\vec{R}_1) , \quad l=0,2,4 \qquad (21)$$

and

$$K_2=\sum_{k\neq1}\kappa_2(\vec{R}_k,\vec{R}_1) , \qquad (22)$$

with

$$\gamma_l(\vec{R}_k,\vec{R}_1)=\int v_l(r_{k1})\phi(\vec{r}_k-\vec{R}_k)\phi(\vec{r}_1-\vec{R}_1)d\vec{r}_kd\vec{r}_1 , \qquad (23)$$

and

$$\kappa_2(\vec{R}_k,\vec{R}_1)= \int w_2(r_{k1})\phi(\vec{r}_k-\vec{R}_k)$$

$$\times \phi(\vec{r}_1-\vec{R}_1)P_2(\hat{r}_{k1}\cdot\hat{n})d\,\vec{r}_k d\,\vec{r}_1 \ . \tag{24}$$

The Appendix derives these results for a cylindrically symmetrical $\phi(\vec{r}-\vec{R})$.

D. Reduction of self-consistent equations

The lattice that we choose to work with is the simplest possible which can accommodate a nematic arrangement that accounts for anisotropic steric effects: a lattice of rectangular parallelepiped cells, each of volume $d_x d_y d_z = d_x^2 d_z = 1/\rho$. In an earlier paper[9] we performed a similar calcualtion as described here without the presence of $w_2(r)$ terms in the potential. In that case, the absence

of anisotropic steric effects means, e.g., a parallel pair of molecules cannot distinguish a side-by-side configuration from an end-to-end configuration. If placed in cells on a rectangular lattice, the most stable lattice would be cubic $(d_x = d_y = d_z)$ by symmetry arguments. Now that $w_2(r)$ terms have entered our model, this will no longer be the case. We shall have to consider rectangular lattices of all proportions, d_z/d_x, in order to determine which structure is thermodynamically the most stable.

Likewise, instead of employing a spherically symmetrical $\phi(\vec{r}-\vec{R})$, as in Ref. 9, we must now use a cylindrically symmetric form, the simplest one being

$$\phi(\vec{r}-\vec{R})= \frac{\alpha^2\gamma}{\pi^{3/2}}e^{-\alpha^2[(x-X)^2+(y-Y)^2]-\gamma^2(z-Z)^2} \ . \tag{25}$$

For this form of $\phi(\vec{r}-\vec{R})$

$$G_l= \frac{4\sqrt{2}\alpha^2\gamma a_l}{\pi^{3/2}}\int_0^\infty dq_x dq_y dq_z e^{-(\beta^2+\alpha^2/2)(q_x^2+q_y^2)-(\beta^2+\gamma^2/2)q_z^2}M(q_x,q_y,q_z\mid\alpha^2,\gamma^2) \ , \tag{26}$$

and

$$K_2= \frac{2\sqrt{2}\alpha^2\gamma b_2}{\pi^{3/2}}\int_0^\infty dq_x dq_y dq_z e^{-(\beta^2+\alpha^2/2)(q_x^2+q_y^2)-(\beta^2+\gamma^2/2)q_z^2}\left[\frac{3q_z^2}{q_x^2+q_y^2+q_z^2}-1\right]M(q_x,q_y,q_z\mid\alpha^2,\gamma^2) \ , \tag{27}$$

where

$$M(q_x,q_y,q_z\mid\alpha^2,\gamma^2)= e^{-\alpha^2 d_x^2/2}(\cosh\alpha^2 d_x q_x+\cosh\alpha^2 d_x q_y)+e^{-\gamma^2 d_z^2/2}\cosh\gamma^2 d_z q_z$$

$$+2e^{-\alpha^2 d_x^2/2}[e^{-\alpha^2 d_x^2/2}\cosh\alpha^2 d_x q_x \cosh\alpha^2 d_x q_y$$

$$+e^{-\gamma^2 d_z^2/2}(\cosh\alpha^2 d_x q_x+\cosh\alpha^2 d_x q_y)\cosh\gamma^2 d_z q_z]$$

$$+4e^{-\alpha^2 d_x^2-\gamma^2 d_z^2/2}\cosh\alpha^2 d_x q_x \cosh\alpha^2 d_x q_y \cosh\gamma^2 d_z q_z+\cdots \ . \tag{28}$$

Equations (18)—(20) and (26)—(28) form a self-consistency loop for $Q(\hat{\Omega})$, given $\phi(\vec{r}-\vec{R})$ as in Eq. (25). Next, from Eqs. (12) and (19), using the addition theorem, the Appendix yields

$$\bar{v}(i,j)=v_0(r_{ij})+v_2(r_{ij})\sigma_2^2+v_4(r_{ij})\sigma_4^2+2w_2(r_{ij})\sigma_2 P_2(\hat{r}_{ij}\cdot\hat{n}) \ , \tag{29}$$

for use in Eq. (16). And thus

$$V(\vec{r}-\vec{R})\equiv V(\vec{u}\mid\alpha,\gamma)= \frac{2\alpha^2\gamma}{\pi^{3/2}}\int_{-\infty}^\infty dq_x dq_y dq_z\left[a_0+a_2\sigma_2^2+a_4\sigma_4^2+b_2\sigma_2\left[\frac{3q_z^2}{q_x^2+q_y^2+q_z^2}-1\right]\right]$$

$$\times e^{-\beta^2(q_x^2+q_y^2+q_z^2)}e^{-\alpha^2(q_x+u_x)^2-\alpha^2(q_y+u_y)^2-\gamma^2(q_z+u_z)^2}$$

$$\times M(q_x+u_x,q_y+u_y,q_z+u_z\mid 2\alpha^2,2\gamma^2) \ . \tag{30}$$

Substituting Eq. (30) into Eq. (15) and taking moments with Eq. (25), we find

$$\frac{1}{\alpha^2}= \frac{2}{Z_\phi}\int u_x^2 e^{-V(\vec{u}\mid\alpha,\gamma)/kT}d\vec{u} \ , \tag{31}$$

and

$$\frac{1}{\gamma^2}= \frac{2}{Z_\phi}\int u_z^2 e^{-V(\vec{u}\mid\alpha,\gamma)/kT}d\vec{u} \ . \tag{32}$$

Equations (30)—(32) form a self-consistency loop for $\phi(\vec{r}-\vec{R})$, in the form of coupled equations for α and γ, given σ_l as in Eq. (19). The two self-consistency loops are intricately intertwined. We shall show how they are solved numerically in Sec. III.

E. Helmholtz free energy

Substitute into Eq. (11) the self-consistency solutions for the nematic and isotropic phases; i.e., treat Eq. (11) term

by term using Eqs. (29), (23), (24), (21), (22), (18), (19), (15), and (16), in that order. The Helmholtz free energies reduce to

$$F_N = F_0 - \frac{N}{2}G_0^N - \frac{3N}{2}(G_2^N \sigma_2^2 + G_4^N \sigma_4^2) - 2NK_2 \sigma_2$$
$$- NkT \ln Z_Q^N - NkT \ln Z_\phi^N , \qquad (33)$$

and

$$F_I = F_0 - \frac{N}{2}G_0^I - NkT \ln Z_Q^I - NkT \ln Z_\phi^I . \qquad (34)$$

These expressions will be used to determine which phase is more stable, and, in turn, the phase-transition temperature *at constant density*.

III. CALCULATIONS FOR MBBA

A. Outline

Much information is available for the nematic liquid crystal MBBA. We apply our present molecular theory to a calculation of its properties.

In several earlier papers[5,8,9] we performed molecular theoretical calculations for MBBA without the inclusion of anisotropic steric terms in the pairwise potential. Reference 9 gives an outline of the procedure when a cell approximation is employed. It may be worthwhile to first read Sec. IV of that reference.

Let us sort out the many parameters in this theory. First of all, for model building we have in Eq. (2) five potential parameters: a_0, a_2, a_4, b_2, and β. We need to seek a combination of these parameters which will yield the correct phase-transition temperature T_{IN} and order parameter σ_2 at T_{IN} at a given density ρ. From experiment, at $\rho = 0.002\,315$ Å^{-3}, $T_{IN} = 317-318$ K and $\sigma_2(T_{IN}) = 0.33-0.34$. Since phase transitions occur under rather stringent conditions, it is not necessarily an easy matter to fit these data even with several parameters—a fact that will soon become appreciated. In our case, we shall restrict β to values close to $\rho^{1/3}$, a_0 to positive values, and

a_2 to negative values, for obvious physical reasons.

There are several thermodynamic variables. ρ and T will be chosen as independent variables. The ratio d_z/d_x will also be varied independently; the value that offers a minimum Helmholtz free energy dictates a thermodynamically stable spatial structure. Nematic and isotropic phases will, of course, prefer different spatial structures since they respond differently to steric effects. In particular, the optimum value of d_z/d_x for the isotropic phase is necessarily unity. For every given ρ, calculations need to be carried out for a range of T and a range of d_z/d_x.

Parameters to be determined by the self-consistency equations, for every set of the potential parameters and every set of the thermodynamic variables, include G_2, G_4, and K_2 in $Q(\hat{\Omega})$, and α and γ in $\phi(\vec{r} - \vec{R})$.

B. Actual procedure

Actual calculations employ a procedure designed to minimize computation. We begin with the recognition that any set of the paramters (G_2, G_4, K_2) would solve the self-consistency equation for $Q(\hat{\Omega})$, thus: Take at given T

$$\xi_2 = \frac{G_2 \sigma_2}{kT} ,$$

$$\xi_4 = \frac{G_4 \sigma_4}{kT} , \qquad (35)$$

$$\zeta_2 = \frac{K_2}{kT} .$$

Use them in Eqs. (18), (20), and (19) to calculate σ_2 and σ_4. Then the values $(G_2 = \xi_2 kT/\sigma_2$, $G_4 = \xi_4 kT/\sigma_4$, $K_2 = \zeta_2 kT)$ can be identified immediately as the set that solves the self-consistency and yields that particular pair of order parameters. By tabulating (ξ_2, ξ_4, ζ_2) with their corresponding (σ_2, σ_4), one thus infers self-consistent sets of (G_2, G_4, K_2). Table I shows a typical segment of the table. If one wishes to fix σ_2 at, e.g., its experimental value, one chooses the line which contains that value for σ_2, i.e., one of the lines marked with asterisks. Such choices are, of course, far from unique. They permit us to

TABLE I. Typical segment of tabulated results for the solution of the self-consistency equation for $Q(\hat{\Omega})$.

	$\xi_2 \equiv \dfrac{G_2\sigma_2}{kT}$	$\xi_4 \equiv \dfrac{G_4\sigma_4}{kT}$	$\zeta_2 \equiv \dfrac{K_2}{kT}$	σ_2	σ_4	G_4/G_2	K_2/G_2
	-0.90	0.99	-1.26	0.367	-0.025	15.954	0.514
	-0.90	0.99	-1.16	0.351	-0.031	11.419	0.453
*	-0.90	0.99	-1.06	0.335	-0.042	8.787	0.395
	-0.90	0.99	-0.96	0.319	-0.050	7.063	0.340
	-0.90	0.99	-0.86	0.303	-0.057	5.845	0.289
	-0.90	0.99	-0.76	0.286	-0.064	4.935	0.242
	-1.08	1.78	-1.32	0.339	-0.112	5.017	0.415
	-1.08	1.78	-1.31	0.338	-0.112	4.968	0.410
	-1.08	1.78	-1.30	0.337	-0.113	4.919	0.405
*	-1.08	1.78	-1.29	0.335	-0.114	4.871	0.401
	-1.08	1.78	-1.28	0.334	-0.114	4.824	0.396
	-1.08	1.78	-1.27	0.333	-0.115	4.778	0.392

TABLE II. Typical segment of tabulated results for the solution of the self-consistency equation for $\phi(\vec{r}-\vec{R})$.

	a_0	a_2	a_4	b_2	α_{in}	α_{out}	γ_{in}	γ_{out}
	383.21	−239.69	−2106.04	−4960.65	1.8180	1.8170	0.8670	0.8654
	395.01	−239.69	−2106.04	−4960.65	1.8180	1.8175	0.8670	0.8662
*	407.47	−239.69	−2106.04	−4960.65	1.8180	1.8180	0.8670	0.8670
	419.88	−239.69	−2106.04	−4960.65	1.8180	1.8184	0.8670	0.8677
	430.86	−239.69	−2106.04	−4960.65	1.8180	1.8190	0.8670	0.8685

move on to meeting other conditions.

Equation (26) indicates that once the ratio G_4/G_2 is known, so is a_4/a_2. [For that matter, $G_0/G_2=a_0/a_2$. But the self-consistency equation for $Q(\hat{\Omega})$ says nothing about G_0. So a_0 is still left free.] This is the case for whatever values are taken on by α and γ, since the integral in Eq. (26) is common for all G_l. Unfortunately, the same is not true for K_2. The integral in Eq. (27) differs from that in Eq. (26). So the ratio b_2/a_2 as determined by K_2/G_2 comes out differently for different pairs of (α,γ). For fixed (α,γ), however, once K_2/G_2 is known, so is b_2/a_2.

Take one of the asterisked lines in Table I. Choose a pair of (α,γ) as input to Eq. (30): $(\alpha_{in},\gamma_{in})$, but use them first in $M(q_x,q_y,q_z \mid \alpha_{in}^2,\gamma_{in}^2)$ and in the integrals of Eqs. (26) and (27). The values of (G_2,G_4,K_2) from that line uniquely determine (a_2,a_4,b_2), leaving a_0 the only undetermined potential parameter. For every choice of a_0 entered into the right-hand side of Eq. (30), Eqs. (31) and (32) yield a pair of output (α,γ): $(\alpha_{out},\gamma_{out})$. Table II shows a list of a_0, $(\alpha_{in},\gamma_{in})$, and $(\alpha_{out},\gamma_{out})$. The line marked with an asterisk indicates an a_0 which yields a solution of the self-consistency equation for $\phi(\vec{r}-\vec{R})$. It should be noted that most lines from Table I would yield no solution at all, *whatever the a_0.*

We thus collect an entire set of potential parameters (a_0,a_2,a_4,b_2,β) which offer solutions to both self-consistency equations and provide the right σ_2, in one thermodynamic environment: $(\rho,T,d_z/d_x)$. For the same potential, we now try different values of d_z/d_x. In each case we re-solve the self-consistency equations, and in each case we obtain the Helmholtz free energies that correspond to the solutions. For the nematic phase, a minimum in the latter with respect to d_z/d_x is sought and compared to the isotropic free energy (at $d_z/d_x=1$). This process is repeated for a range of values of T. The condition $F_N=F_I$ determines T_{IN}^*, the transition temperature at constant density.

It is, of course, highly unlikely that T_{IN}^* would turn out to fall in the range 316–317 K, which corresponds[10,11] to a T_{IN} of 317–318 K. So the *entire* process must be repeated for a new asterisked line in (an extended) Table I. If and when a line that gives the right T_{IN}^* is eventually located, we will carry out the calculation for a range of T about T_{IN}^* to ascertain that, indeed, a transition has taken place at the right temperature, and for obtaining temperature-dependent properties. Table III displays calculated results for $\rho=0.002\,315$ and $0.002\,317$ Å^{-3}. In

certain ranges of temperatures, several densities will be studied to obtain density-dependent properties.

IV. RESULTS AND DISCUSSIONS

A. Potential parameters

The set of potential parameters determined as a best fit to the transition temperature and the order-parameter discontinuity is

$$a_0/k = 407.47 \text{ K} ,$$

$$a_2/k = -239.69 \text{ K} ,$$

$$a_4/k = -2106.04 \text{ K} ,$$

$$b_2/k = -4960.65 \text{ K} ,$$

$$\beta = 0.132 \text{ Å}^{-1} .$$

It is reasonable to inquire of the physical meaning of these parameters. a_0, a_2, and a_4 are familiar potential parameters in the liquid-crystal literature.[4,5] Had the r dependence of $v_l(r)$ been more realistic, e.g., containing a hard core, we might regard them as expansion coefficients and require that they fall off with increasing l. But just as in other molecular theoretical calculations referred to in this paper, our model is much too crude to yield a sound physical interpretation. The best that one can say is that it is the simplest empirical formula that can be constructed to fit thermodynamic data.

We are more certain of the meaning of b_2 since it represents the only anisotropic contribution to the pairwise potential. It contains short-range anisotropic steric

TABLE III. Summary of results at two densities.

ρ (Å^{-3})	T (K)	σ_2	σ_4	$(F_N-F_I)/Nk$ (K)
0.002 314	313.2	0.380	−0.030	−1.11
	315.2	0.367	−0.033	−0.39
	316.2	0.354	−0.037	−0.02
$T_{IN}^* \rightarrow$	316.3	0.352	−0.038	0.00
	317.2	0.335	−0.044	0.19
	318.0	0.306	−0.047	0.32
0.002 317	316.2	0.355	−0.037	−0.06
$T_{IN}^* \rightarrow$	316.7	0.352	−0.038	0.00
	317.2	0.346	−0.042	0.12
	318.0	0.338	−0.047	0.27

effects. That b_2 turns out to be so large should not be surprising for the following reason. If we are to "translate" pair interactions in a hard-rod model to potential formulas such as Eq. (1), the anisotropic term $w_2(r)$ will be totally overwhelming. In another study, we have been attempting to reconcile the hard-rod and potential models through numerical comparisons of the resulting potential profiles when parameters in both models are varied. We found that $w_2(r)$ invariably turns out to be large, even for rods whose length-to-diameter ratio lies between two and three.[7] The results of that study will be published elsewhere.

The reader is cautioned against thinking of this work as an attempt to do a realistic theory from first principles. That would be much too ambitious at this stage. What we present here is merely a model calculation which illustrates and stresses the importance of anisotropic steric forces in the molecular theory of liquid crystals.

B. Order parameters

From Table III we find that at $T_{IN}^* = 316.3$ K, $\sigma_2 = 0.352$, and $\sigma_4 = -0.038$. However, as $T_{IN} - T_{IN}^* \approx 0.8 - 1.0$ K,[10,11] we take $T_{IN} = 317.2$ K. At that temperature, $\sigma_2 = 0.335$ and $\sigma_4 = -0.044$.

This is an exciting result, for, to our knowledge, it is the first time that a molecular theory can yield a *stable* nematic phase which possesses a *negative* σ_4 at T_{IN}. Experimental data[12,13] place this value at a point far more negative. Nevertheless, we feel that relating negative σ_4 to anisotropic steric effects has moved us one step in the right direction.

Next, we discuss the temperature dependence of the order parameters. The entries in Table III should not be directly compared to experiment. Table III was obtained for a constant density, while experimental results are usually for a constant pressure, 1 atm. For MBBA, we use data obtained by Gulari and Chu,[14] interpolated and scaled to give $\rho = 0.002\,320$ Å^{-3} at $T = 317.2$ K—our calculated T_{IN}. Table IV shows our calculated results. The last two columns are also plotted in Fig. 1 and compared to data from Refs. 12 and 13, as well as to results calculated without the anisotropic steric potential.[9] There seems to be an improvement, in that the temperature dependence is now stronger, but the improvement is slight at best.

C. Density dependence of transition temperature

Table III indicates that at transition under different densities, σ_2 and σ_4 remain unchanged. This is consistent with experimental findings.[15] Note that σ_2 and σ_4 vary
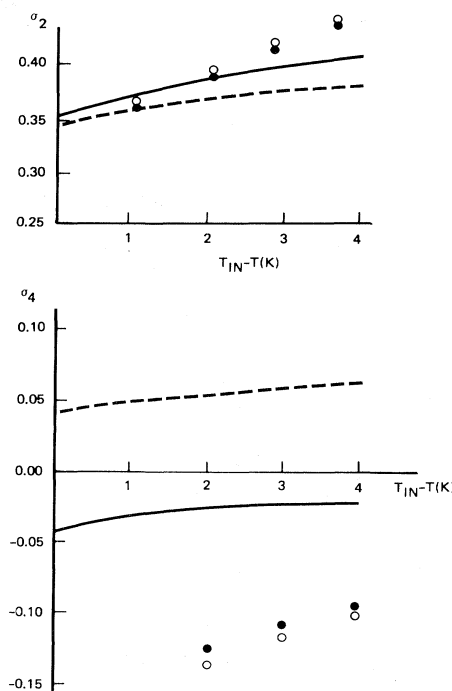

FIG. 1. Order parameters σ_2 and σ_4 as functions of temperature. O, Ref. 12; ●, Ref. 13; $-\,-\,-$, Ref. 8 (theoretical curve without anisotropic steric potentials); ———, present work.

quite strongly with ρ and T, so the fact that they remain unchanged at transition cannot be taken as a foregone conclusion.

From Table III one can also estimate the parameter $\Gamma \equiv d \ln T_{IN}(\rho)/d \ln \rho$. It turns out to be about 1.5. This is a slight improvement over the 1.26 obtained without anisotropic steric potentials,[8] but nowhere near the experimental value[16] of 4.7.

D. Volume change

Figure 2 is a graphic aid for carrying out a Maxwell construction:

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

$$= - \left[\frac{\partial (F_I - F_N)/N}{\partial v} \right]_T$$

$$= \left[\frac{\partial (F_N - F_I)/N}{\partial v} \right]_T .$$

TABLE IV. Results under constant pressure. $P = 1$ atm.

T (K)	$T_{IN} - T$ (K)	v (Å^3)	ρ (Å^{-3})	d_x (Å)	d_z (Å)	σ_2	σ_4
317.2	0.0	431.05	0.002 320	5.899	12.384	0.352	−0.041
316.2	1.0	430.50	0.002 323	5.896	12.382	0.371	−0.034
315.2	2.0	430.07	0.002 325	5.895	12.379	0.387	−0.030
314.2	3.0	429.66	0.002 327	5.893	12.375	0.394	−0.028
313.2	4.0	429.28	0.002 329	5.891	12.371	0.398	−0.026

From Table III we find at $T = 317.2$ K,

$$P_C - P_A = \frac{0.12 - 0.19}{\dfrac{1}{0.002\,317} - \dfrac{1}{0.002\,315}} = 0.188 \text{ k\AA}^{-3} .$$

But from thermodynamics $\Delta v/v \approx K_T(P_C - P_A)$, where K_T denotes the isothermal compressibility, and for MBBA,[16] $K_T = 4.87 \times 10^{-11}$ cm^2/dyn. Thus $\Delta v/v \approx 0.126\%$, in good agreement with the experimental value[14,17] of 0.11 to 0.14%.

E. Latent heat

The entropy change at transition at constant density is given by

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

$$= - \left[\frac{\partial(F_I - F_N)/N}{\partial T} \right]_\rho$$

$$= \left[\frac{\partial(F_N - F_I)/N}{\partial T} \right]_\rho .$$

From Table III we find at $\rho = 0.002\,315$ \AA^{-3},

$$S_C - S_A = \frac{0.32 - (-0.02)}{318.0 - 316.2} = 0.189k .$$

But the latent heat per particle is given by $T \Delta S$, or

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

$$\approx (\beta_P T/K_T)\Delta v + T(S_C - S_A) .$$

Taking the coefficient of thermal expansion β_T to equal[14] 8.7×10^{-4} K^{-1} and K_T and Δv from above, we find $\Delta H \approx 684$ J/mole, significantly smaller than the 833 J/mole obtained without anisotropic steric potentials,[8] but still a factor of 2 larger than the experimental value[18,19] of
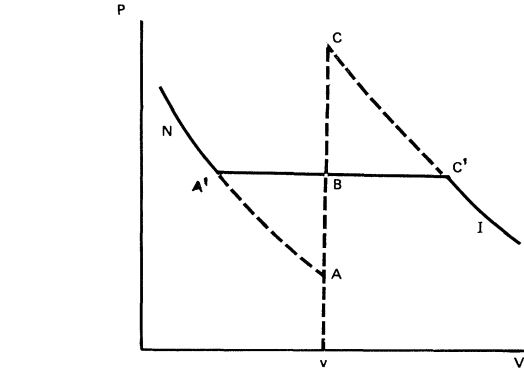

FIG. 2. Graphic aid for carrying out a Maxwell construction.

284–381 J/mole.

In summary, we find that our most significant gain with the inclusion of anisotropic steric terms in the intermolecular potential is a negative σ_4. All other properties have moved somewhat toward experimental results. Referring back to the discrepancies listed in Sec. I, even though we have not been able to account for them, it must be considered fortunate and encouraging that all changes have moved in the right direction.

We intend to use the new potential determined here in a full-fledged OAPC calculation. The latter formalism including anisotropic steric potentials was outlined in Ref. 7. It is more suitable than the cell approximation for a liquid.

APPENDIX: DERIVATION OF SELF-CONSISTENT EQUATIONS

The starting point is Eq. (11). By introducing a Lagrange multiplier λ_ϕ along with Eq. (14) and varying $\mathscr{F}\{Q, \phi\}$ with respect to $\phi(\vec{r} - \vec{R})$, one obtains immediately Eqs. (15)–(17). $\bar{v}(i,j)$ reads

$$\bar{v}(i,j) = \int \{ v_0(r_{ij}) + v_2(r_{ij})P_2(\hat{\Omega}_i \cdot \hat{\Omega}_j) + v_4(r_{ij})P_4(\hat{\Omega}_i \cdot \hat{\Omega}_j) + w_2(r_{ij})[P_2(\hat{\Omega}_i \cdot \hat{r}_{ij}) + P_2(\hat{\Omega}_j \cdot \hat{r}_{ij})] \} Q(\hat{\Omega}_i)Q(\hat{\Omega}_j) d\hat{\Omega}_i d\hat{\Omega}_j .$$

The addition theorem

$$P_l(\hat{\Omega}_i \cdot \hat{\Omega}_j) = P_l(\hat{\Omega}_i \cdot \hat{n})P_l(\hat{\Omega}_j \cdot \hat{n}) + 2 \sum_{m=1}^{l} \frac{(l-m)!}{(l+m)!} P_l^m(\hat{\Omega}_i \cdot \hat{n})P_l^m(\hat{\Omega}_j \cdot \hat{n})\cos m(\varphi_{\Omega_i} - \varphi_{\Omega_j}) ,$$

together with the assumption that $Q(\hat{\Omega}) = Q(\hat{\Omega} \cdot \hat{n})$, reduces $\bar{v}(i,j)$ to its form in Eq. (29).

By introducing another Lagrange multiplier λ_Q to go with Eq. (13) in the variation of $\mathscr{F}\{Q, \phi\}$, one finds

$$\frac{\delta \mathscr{F}\{Q, \phi\}}{\delta Q(\hat{\Omega}_1)} = 0 = \sum_{i \neq 1} \int v(i,1)Q(\hat{\Omega}_i)\phi(\vec{r}_i - \vec{R}_i)\phi(\vec{r}_1 - \vec{R}_1)d\hat{\Omega}_i d\vec{r}_i d\vec{r}_1 + kT[\ln Q(\hat{\Omega}_1) + 1] + \lambda_Q . \tag{A1}$$

Under the assumption $Q(\hat{\Omega}) = Q(\hat{\Omega} \cdot \hat{n})$, the integral in the above expression reduces to

$$\gamma_0 + \gamma_2 \sigma_2 P_2(\hat{\Omega}_1 \cdot \hat{n}) + \gamma_4 \sigma_4 P_4(\hat{\Omega}_1 \cdot \hat{n}) + \kappa_2 \sigma_2 + \chi_2 , \tag{A2}$$

where

$$\kappa_2 = \int w_2(r_{i1})\phi(\vec{r}_i - \vec{R}_i)\phi(\vec{r}_1 - \vec{R}_1)P_2(\vec{r}_{i1} \cdot \hat{n})d\vec{r}_i d\vec{r}_1 , \tag{A3}$$

and

$$\chi_2 = \int w_2(r_{i1})\phi(\vec{r}_i - \vec{R}_i)\phi(\vec{r}_1 - \vec{R}_1)P_2(\hat{r}_{i1} \cdot \hat{\Omega}_1)d\vec{r}_i d\vec{r}_1 \ . \tag{A4}$$

It becomes necessary to demonstrate that $\sum_{i \neq 1} \chi_2(\vec{R}_i, \vec{R}_1)$ depends only on $(\hat{\Omega}_1 \cdot \hat{n})$.

While undoubtedly a general proof should exist for any cylindrically symmetrical $\phi(\vec{r} - \vec{R})$, we examined a special case: a rectangular parallelepiped lattice structure with the long axis in the z direction and $\phi(\vec{r} - \vec{R})$ as given in Eq. (25). α and γ measure the extent of molecular excursion in the lateral and longitudinal directions, respectively.

Now, using the addition theorem

$$\chi_2 = \kappa_2 P_2(\hat{\Omega}_1 \cdot \hat{n}) + \tfrac{1}{3}(w_2^{1c}\cos\varphi_{\Omega_1} + w_2^{1s}\sin\varphi_{\Omega_1})P_2^1(\hat{\Omega}_1 \cdot \hat{n})$$

$$+ \tfrac{1}{12}(w_2^{2c}\cos2\varphi_{\Omega_1} + w_2^{2s}\sin2\varphi_{\Omega_1})P_2^2(\hat{\Omega}_1 \cdot \hat{n}) \ , \tag{A5}$$

where

$$w_2^{mc} = \int w_2(r_{i1})\phi(\vec{r}_i - \vec{R}_i)\phi(\vec{r}_1 - \vec{R}_1)P_2^m(\hat{r}_{i1} \cdot \hat{n})$$

$$\times \cos(m\varphi_{r_{i1}})d\vec{r}_i d\vec{r}_1 \ , \tag{A6}$$

and

$$w_2^{ms} = \int w_2(r_{i1})\phi(\vec{r}_i - \vec{R}_i)\phi(\vec{r}_1 - \vec{R}_1)P_2^m(\hat{r}_{i1} \cdot \hat{n})$$

$$\times \sin(m\varphi_{r_{i1}})d\vec{r}_i d\vec{r}_1 \ , \tag{A7}$$

for $m = 1, 2$. By transforming to center-of-mass and relative coordinates, it can be shown that

$$\sum_{i \neq 1} w_2^{1c} = \sum_{i \neq 1} w_2^{1s} = \sum_{i \neq 1} w_2^{2c} = \sum_{i \neq 1} w_2^{2s} = 0 \ . \tag{A8}$$

We actually demonstrated this fact for six nearest-neighbor shells.

Equations (A1)—(A8) thus permit $Q(\hat{\Omega})$ to be expressed as in Eqs. (18)—(24). Straightforward algebra leads to Eqs. (26)—(28), where contributions from three nearest-neighbor shells are explicitly displayed. For the densities considered, the spread in $\phi(\vec{r} - \vec{R})$ turns out to be such that it quite suffices to consider just those three shells.

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