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Molecular Theory of Liquid Crystals Including Anisotropic Repulsion

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Molecular Theory of Liquid Crystals Including Anisotropic Repulsion†

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We summarize in this report our progress on constructing a molecular theory for liquid crystals using models which include anisotropic intermolecular forces. In terms of cylindrically symmetric non-chiral molecules, whose pairwise interactions depend on the scalars r_{ij}, $\hat{\Omega}_i \cdot \hat{\Omega}_j$, $\hat{\Omega}_i \cdot \hat{r}_{ij}$, and $\hat{\Omega}_j \cdot \hat{r}_{ij}$, this means the introduction of $\hat{\Omega} \cdot \hat{r}$ terms explicitly into the formulation of the Hamiltonian. In the mean field treatment, such terms contribute nothing to the nematic phase. In a more sophisticated theory such as our OAPC, to be described below, such terms in the Hamiltonian bring with them non-trivial mathematical complications and significant physical effects.

In the OAPC (*o*rientational *a*veraged *p*air *c*orrelation) theory, liquid structures are brought into consideration through methods well known from the theory of classical liquids, while the orientational order is treated in a mean-field-like manner. The physical basis for such a theory is obvious: at liquid crystalline densities one can hardly justify the neglect of short-range spatial correlations. In earlier work involving one of the authors, OAPC was applied to models whose Hamiltonians depend on r_{ij} and $\hat{\Omega}_i \cdot \hat{\Omega}_j$. Certain improvements on the calculation of isotropic-nematic transition properties over mean field theories were seen. The discrepancies that remain can probably be traced to the neglect of the anisotropic $\hat{\Omega} \cdot \hat{r}$ terms. We have now succeeded to work out the mathematics for models including $\hat{\Omega} \cdot \hat{r}$ potentials, find ways to relate the associated potential parameters to the parameters describing soft-core cylindrical molecules, determine changes in the calculated results for cases of weak anisotropic forces, and build up computer programs for solving integral equations that govern cases of strong anisotropic repulsions.

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We present here a description of the models, a brief outline of the theory, and preliminary numerical results for weakly anisotropic models chosen to mimic PAA. We summarize present work in progress and indicate directions for future effort.

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I INTRODUCTION

Since the mean field theoretical calculation of Maier and Saupe,[1] there have been a number of papers published on the subject of molecular theory of liquid crystals. Earlier work included series of papers by Kobayashi,[2] McMillan,[3] our own group[4-7] Sheng and Wojtowicz,[8] and many others.[9] All these calculations employed potential models which do not take into account anisotropic steric effects. The results were often qualitatively different from those obtained with hard rod models.[10-13] We have tried to deal with steric effects by introducing anisotropic terms into our potential model. This is a progress report on our recent efforts.

In two previous papers[14,15] from our group, we described a molecular theory of nematic liquid crystals which takes into account short-range spatial correlations between molecules in an approximate way. The approximation calls for treating orientational correlations by mean field while letting spatial correlations enter through orientation-averaged pair correlations functions (OAPC).

In the first paper[14] (hereafter referred to as I), it was shown that, given a pairwise potential of the simple form

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

where $\mathbf{r}$ and $\hat{\Omega}$ denote the position and orientation vectors of a cylindrically symmetric molecule, the formalism for obtaining the one- and two-particle distribution functions reduces to a two-fold self-consistency scheme. Numerical computations were then carried out in a prototype calculation for para-azoxyanisole (PAA), in which the potential parameters were determined by fitting the clearing point to experimental data. For this very crude model, we found *qualitative* agreement between theoretical and experimental results. Upon closer inspection, however, we noticed that the order parameter discontinuity at isotropic-nematic transition was too large and its temperature dependence too weak. A plot of the transition temperature against the specific volume, ln T_{IN}-versus- ln v, did yield a straight line, but at a slope, Γ, of -1.45 instead of the experimental value of -4.0. At transition, the fractional volume change ($\Delta v/v$) was found to be 0.714%, and the latent heat (ΔH) 2448J/mole, both of them much too large compared to the experimental values of 0.30–0.36% and 574-760J/mole, respectively. We were nevertheless comforted by the fact that these quantities all had the right order of magnitude, and that certain improvements lie in an obvious direction.

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The theory as it stood was plagued by a weak link in the formalism; the Helmholtz free energy had to be calculated with an expression obtained by identifying its Euler-Lagrange equation to the generalized Bogoliubov-Born-Green-Kirkwood-Yvon equation (BBGKY) for the density function. Such a "trick" is physically pleasing but mathematically unsound. In our second paper[15] (hereafter referred to as II), the theory was reformulated in a rigorous fashion. The free energy formula obtained in OAPC was shown to be identical to that derived in I. This was one major contribution of II.

Also in II we took the first obvious step toward improving *quantitative* aspects of the theory. The pairwise potential was taken to include a P_4 term:

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

Parameters in $v_0(r)$, $v_2(r)$, and $v_4(r)$ were determined by fitting to data the order parameter discontinuity as well as the transition temperature. Numerical computations were carried out for PAA and methoxybenzylidene butylaniline (MBBA). The temperature dependence of the order parameter remains too weak, and Γ, the slope of the $\ln T_{IN} - \ln v$ line, became even smaller in magnitude. However, there were significant improvements in all other transition properties. For PAA, $\Delta v/v$ and ΔH came out as 0.46% and 1452J/mole, respectively. For MBBA, these quantities were found to be 0.13% and 833J/mole, in comparison with the experimental values of 0.11–0.14% and 284–381J/mole.

In all this work, we recognized that unless anisotropic steric effects are allowed to play a proper role there will remain sizable discrepancies in some of the physical propeties. To this end, our recent efforts have been directed toward two goals. First, we are exhaustively examining potentials of the type

$$v(1,2) = v_0(r_{12}) + v_2(r_{12})P_2(\hat{\Omega}_1 \cdot \hat{\Omega}_2) + \cdots + w_2(r_{12})[P_2(\hat{\Omega}_1 \cdot \hat{r}_{12}) + P_2(\hat{\Omega}_2 \cdot \hat{r}_{12})] + \cdots, \tag{3}$$

to see what forms $v_0(r)$, $v_2(r)$, $w_2(r)$, . . . must assume in order to mimic potentials between hard cylinders. (By hard cylinders we actually include soft cylinders, spongy cylinders, and cylinders with sticky outer layers.) At the same time, we work out the mathematical formalism for potentials of the type (3), using in our preliminary attempts simple forms of $v_0(r)$, $v_2(r)$, $w_2(r)$, . . . which are not expected to be realistic. A previous paper[16] applied the mean field approximation to (3). Since then we have worked out complete mathematical details for applying OAPC to (3). These results will be published elsewhere. In the meantime, we examine several weak-anisotropy cases (w_2 weak in comparison to v_0 and v_2) and carry out numerical computations for these models. In such limiting cases, the orientation-averaged pair correlation function is obtained not by solving the full integral equation, but by an expansion procedure. The latter, then, give rise to the contents of the present paper.

II FORMALISM

We assume N molecules in volume V, so that the density is given by $\rho \equiv N/V$. The pairwise potential assumes the form

$$v(1,2) = v_0(r_{12}) + v_2(r_{12})P_2(\hat{\Omega}_1 \cdot \hat{\Omega}_2) + w_2(r_{12})[P_2(\hat{\Omega}_1 \cdot \hat{r}_{12}) + P_2(\hat{\Omega}_2 \cdot \hat{r}_{12})].$$

As in II, we define the Helmholtz free energy functional at ρ and T as:

$$\mathcal{F}\{P_N\} = F_0 + \int \left(\sum_{\substack{i<j \\ =1}}^{N} v(i,j) \right) \frac{P_N(1, \ldots, N)}{N!} d1 \ldots dN + kT \int \frac{P_N(1, \ldots, N)}{N!} \ln \frac{P_N(1, \ldots, N)}{N!} d1 \ldots dN, \quad (4)$$

where P_N is a general probability distribution function $P_N(1, \ldots, N) \equiv P_N(\mathbf{r}_1, \hat{\Omega}_1, \ldots, \mathbf{r}_N, \hat{\Omega}_N)$, normalized such that

$$\int P_N(1, \ldots, N) d1 \ldots dN = N! \quad (5)$$

$d1 \ldots dN$ denotes $d\mathbf{r}_1 d\hat{\Omega}_1 \ldots d\mathbf{r}_N d\hat{\Omega}_N$. It was shown that minimizing $\mathcal{F}\{P_N\}$ with respect to $P_N(1, \ldots, N)$ under the constraint (5) gives rise to the classical Boltzmann distribution as anticipated.

In the OAPC, one writes for isotropic and nematic phases:

$$P_N(1, \ldots, N) \approx N! \left(\prod_{i=1}^{N} Q(\hat{\Omega}_i) \right) \phi_N(\mathbf{r}_1, \ldots, \mathbf{r}_N), \quad (6)$$

thus decoupling in such an approximation the orientational and spatial parts of the distribution function. One then optimizes P_N by minimizing the now-approximate free energy functional $\mathcal{F}\{Q, \phi_N\}$ with respect to $Q(\hat{\Omega})$ and $\phi_N(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. The result, when substituted back into Eqs. (6) and (4), yields the equilibrium Helmholtz free energy $F(\rho, T)$, from which come all thermodynamic and transition properties of the system.

With a potential that couples $\hat{\Omega}$ to $\mathbf{r}$, following the above prescription is no longer a trivial matter. We find first of all

$$\phi_N(\mathbf{r}_1, \ldots, \mathbf{r}_N) = Z_r^{-1} \exp\left(-\frac{1}{kT} \sum_{i<j} \bar{v}_{ij} \right), \quad (7)$$

where

$$\bar{v}_{ij} = \bar{u}_{ij} + \bar{w}_{ij}, \quad (8)$$

$$\bar{u}_{ij} = v_0(r_{ij}) + v_2(r_{ij})\sigma_2^2, \quad (9)$$

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$$\bar{w}_{ij} = 2w_2(r_{ij})\sigma_2 P_2(\hat{r}_{ij}\cdot\hat{n}), \tag{10}$$

with $\hat{r}_{ij}\cdot\hat{n}$ denoting the direction cosine between $\hat{r}_{ij}$ and the director $\hat{n}$, and

$$Z_r = \int \exp\left(-\frac{1}{kT}\sum_{i<j}\bar{v}_{ij}\right)d\mathbf{r}, \ldots d\mathbf{r}_N. \tag{11}$$

And σ_2 stands for the usual orientational order parameter:

$$\sigma_2 = \int Q(\hat{\Omega})P_2(\hat{\Omega}\cdot\hat{n})d\hat{\Omega}. \tag{12}$$

Next, we find

$$Q(\hat{\Omega}_i) = Z_\Omega^{-1}\exp\left\{\frac{-\rho}{kT}[\kappa_2\sigma_2 + (\kappa_2 + \gamma_2\sigma_2)P_2(\hat{\Omega}_i\cdot\hat{n})]\right\}, \tag{13}$$

where

$$\gamma_l = \int v_l(r)g(\mathbf{r})d\mathbf{r}, \quad l = 0,2, \tag{14}$$

$$\kappa_2 = \int w_2(r)P_2(\hat{r}\cdot\hat{n})g(\mathbf{r})d\mathbf{r}, \tag{15}$$

$$Z_\Omega \int \exp\left\{\frac{-\rho}{kT}[\kappa_2\sigma_2 + (\kappa_2 + \gamma_2\sigma_2)P_2(\hat{\Omega}\cdot\hat{n})]\right\}d\hat{\Omega}, \tag{16}$$

and

$$g(\mathbf{r}_{12}) = \frac{N(N-1)}{\rho^2}Z_r^{-1}\int \exp\left(\frac{-1}{kT}\sum_{i<j}\bar{v}_{ij}\right)d\mathbf{r}_3 \ldots d\mathbf{r}_N. \tag{17}$$

Equations (7)–(17) should be solved self-consistently. When there is more than one solution, the Helmholtz free energy will be evaluated in each case to determine which of the possible phases: nematic (N) or isotropic (I), is stable. Substituting the self-consistency solutions into Eq. (4) gives

$$F = (F_0 - N\rho\gamma_0) - NkT\ln Z_\Omega - kT\ln Z_r - N\rho(2\kappa_2\sigma_2 + \gamma_2\sigma_2^2). \tag{18}$$

$F = F_N$ when σ_2 is finite, and $F = F_I$ when σ_2 equals 0.

For every choice of the potential functions $v_l(r)$ and $w_2(r)$, and every choice of the thermodynamic variables ρ and T, then, one needs Z_Ω, Z_r, and $g(\mathbf{r})$ to complete the calculation. Given $g(\mathbf{r})$, γ_l, κ_2 and σ_2 are readily available; the integration in Eq. (16) can then be carried out without effort. It turns out that

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Z_r is also relatively simple to evaluate. Differentiating Eq. (11) with respect to σ_2, one finds

$$\frac{d \ln Z_r}{d\sigma_2} = -\frac{N\rho}{kT}(\kappa_2 + \gamma_2\sigma_2). \tag{19}$$

Thus,

$$(\ln Z_r)_N - (\ln Z_r)_I = \int_0^{\sigma_2} \frac{-N\rho}{kT}(\kappa_2 + \gamma_2\sigma_2')d\sigma_2'. \tag{20}$$

To obtain $\ln Z_r$ one needs $\kappa_2(\sigma_2')$ and $\gamma_2(\sigma_2')$, and thus $g(\mathbf{r}\,|\,\sigma_2')$, for a continuous range of σ_2' all the way up to the self-consistent value σ_2. Note that the only physically meaningful order parameter is the one at equilibrium: σ_2. All other values σ_2' are used merely for calculational purposes: They define $g(\mathbf{r}_{12}\,|\,\sigma_2')$ through Eqs. (17) and (8)–(10).

Our task focuses now on calculating $g(\mathbf{r}_{12}\,|\,\sigma_2)$. For every σ_2-dependent $\bar{v}_{ij}$, $g(\mathbf{r}_{12}\,|\,\sigma_2)$ can *in principle* be evaluated as a many body integral. In practice, however, one needs to use an integral equation technique or stochastic methods. In I, we solved an integral equation and obtained $g(r_{12}\,|\,\sigma_2)$ for a central $\bar{v}_{ij}$, namely $\bar{u}_{ij}$. Here, the presence of $\bar{w}_{ij}$, in particular its dependence on the direction of $\mathbf{r}_{ij}$, makes the derivation of the integral equation difficult and the numerical solution most impractical on computers which are available to us. In this paper, we shall consider only weak-anisotropy cases. In other words, we assume w_2 weak compared to v_0 and v_2. More accurately, we assume $\bar{w}_{ij}$ small compared to $\bar{u}_{ij}$. In that case, we can use an expansion scheme to calculate the effect of $\bar{w}_{ij}$ to low orders and estimate the contribution of such "anisotropic perturbations." For most liquid crystals, treating the anisotropy as a perturbation will not be realistic. The work in this paper should only be regarded as a tentative step toward the eventual solution of the integral equation—a subject to be discussed elsewhere.

III LOWEST ORDER EXPANSION OF $g(\mathbf{r}\,|\,\sigma_2)$

We adapt for our use a cluster expansion procedure due originally to van Kampen.[17]

Let us define a generalized normalization integral:

$$\Xi(\beta) = \int \prod_{i<j} e^{\beta X_{ij} + U_{ij} + W_{ij}} d\tau, \tag{21}$$

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where U_{ij} and W_{ij} denote $-\bar{u}_{ij}/kT$ and $-\bar{w}_{ij}/kT$ for short, and $X_{ij} \equiv X(\mathbf{r}_i, \mathbf{r}_j)$ represents some two-particle multiplicative operator whose utility will soon become obvious. β is a parameter. $d\tau$ denotes $d\mathbf{r}_1 \ldots d\mathbf{r}_N$. Later we shall also use the symbol $d\tau_{(i,j,\ldots)}$ to represent differential elements $d\mathbf{r}_1 \ldots d\mathbf{r}_N$ *excluding* $d\mathbf{r}_i d\mathbf{r}_j \ldots$.

Write

$$q_{ij} \equiv e^{\beta X_{ij} + W_{ij}}, \tag{22}$$

and define a cluster average with $\prod_{i<j} e^{U_{ij}}$ as weight:

$$\overline{A(1,2,\ldots,\nu)} \equiv \int A(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_\nu) \prod_{i<j} e^{U_{ij}} d\tau. \tag{23}$$

Then,

$$\Xi(\beta) = \int \left(\prod_{i<j} q_{ij} \right) \prod_{i<j} e^{U_{ij}} d\tau = \overline{\prod_{i<j} q_{ij}}. \tag{24}$$

From the definition of Ξ, Eq. (21), we find

$$J \equiv \left[\frac{d \ln \Xi(\beta)}{d\beta} \right]_{\beta=0} = \frac{\int \left(\sum_{i<j} X_{ij} \right) \prod_{k<l} e^{U_{kl} + W_{kl}} d\tau}{\int \prod_{k<l} e^{U_{kl} + W_{kl}} d\tau}, \tag{25}$$

which reduces to

$$J = \tfrac{1}{2} \rho^2 \int X_{ij} g(\mathbf{r}_{ij} \mid \sigma_2) d\mathbf{r}_i d\mathbf{r}_j \tag{26}$$

with the aid of Eqs. (8), (11), and (17). Now, if only we can evaluate J by expanding Eq. (24) and taking the derivative of $\ln \Xi(\beta)$ term-by-term, we can use Eq. (26) to extract an expansion formula for $g(\mathbf{r} \mid \sigma_2)$.

In a cluster development, the leading term for $\Xi(\beta)$ is given by

$$\Xi_2(\beta) = \prod_{i<j} \bar{q}_{ij}. \tag{27}$$

Thus, in the same order,

$$J_2 = \sum_{i<j} \frac{1}{(\bar{q}_{ij})_{\beta=0}} \left(\frac{d\bar{q}_{ij}}{d\beta} \right)_{\beta=0} = \sum_{i<j} \frac{\int X_{ij} e^{W_{ij}} \prod_{k<l} e^{U_{kl}} d\tau}{\int e^{W_{ij}} \prod_{k<l} e^{U_{kl}} d\tau}, \tag{28}$$

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and thus

$$\rho^2 g_2(\mathbf{r}_{ij}|\sigma_2) = \frac{\int e^{W_{ij}} \prod_{k<l} e^{U_{kl}} d\tau_{(i,j)}}{\int e^{W_{ij}} \prod_{k<l} e^{U_{kl}} d\tau}$$
$$= \frac{\int e^{W_{ij}} \prod_{k<l} e^{U_{kl}} d\tau_{(i,j)}}{\int \prod_{k<l} e^{U_{kl}} d\tau \cdot [1 + A]}, \tag{29}$$

where

$$A = \int (e^{W_{ij}} - 1) \frac{\int \prod_{k<l} e^{U_{kl}} d\tau_{(i,j)}}{\int \prod_{k<l} e^{U_{kl}} d\tau} d\mathbf{r}_i d\mathbf{r}_j = 0(N^{-1}) \tag{30}$$

for a short-ranged W_{ij}. Recognizing that

$$g_U(r_{ij}|\sigma_2) \equiv \frac{1}{\rho^2} \frac{\int \prod_{k<l} e^{U_{kl}} d\tau_{(i,j)}}{\int \prod_{k<l} e^{U_{kl}} d\tau} \tag{31}$$

stands for the pair correlation function obtained in I for $\bar{u}_{ij}$, we arrive at the lowest order result:

$$g(\mathbf{r}_{ij}|\sigma_2) \approx g_2(\mathbf{r}_{ij}|\sigma_2) = e^{W_{ij}} g_U(r_{ij}|\sigma_2) = g_U(r_{ij}|\sigma_2) e^{-\bar{w}_{ij}/kT}. \tag{32}$$

This result is most unsurprising. The only reason for carrying out the formal expansion procedure, as we did here, was to show that a systematic cluster development is possible, and Eq. (32) results from such an expansion in a most natural way. Indeed, we have derived the next term in the expansion, which involves the three-particle correlation function of I. To go on to that order would mean doing as much computational work as directly solving the integral equation for $g(\mathbf{r}_{ij}|\sigma_2)$. It would destroy the practical advantage gained in the use of an expansion procedure. We thus stop at Eq. (32), and use $g_U(r_{ij}|\sigma_2)e^{-\bar{w}_{ij}/kT}$ in all calculations requiring $g(\mathbf{r}_{ij}|\sigma_2)$.

IV MODEL CALCULATIONS

In I, we chose for a PAA model

$$v_0(r) = 4\epsilon_0 \left[\left(\frac{a_0}{r}\right)^{12} - \left(\frac{a_0}{r}\right)^{6} \right], \tag{33}$$

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and

$$v_2(r) = -4\epsilon_2\left(\frac{a_2}{r}\right)^6, \tag{34}$$

with

$$\epsilon_0 = 145.426 \text{ k°K},$$

$$\epsilon_2 = 96.950 \text{ k°K},$$

and

$$a_0 = a_2 = 6.348823 \text{ Å}.$$

Here, we take $w_2(r)$ in the same form as $v_2(r)$:

$$w_2(r) = -4\omega_2\left(\frac{a_\omega}{r}\right)^6,$$

where

$$a_\omega = a_0 = 6.348823 \text{ Å}. \tag{35}$$

ω_2 becomes the only potential parameter to undergo adjustment.

We tried three values of ω_2: −9.695, −19.39, and 19.39 k°K, respectively −10%, −20%, and +20% of ϵ_2. In each case, we carried out computations in accordance with the program set forth in previous sections, for overall number densities 0.002667 and 0.002670 A^{-3}, and at a range of temperatures broad enough to include the constant-volume transition temperatures. In order to mimic PAA realistically, we should have varied some other potential parameters to return the transition temperature to about 404.45°K, as in I, which corresponds to an experimental constant-pressure transition temperature of 408°K. We decided against varying the other potential parameters because there is more than one way to vary them, and because variations would mask the direct effect of incorporating anisotropic interaction into our model.

Tables I–III show the results of our calculations. We would like to offer several comments.

First, the inclusion of anisotropic terms in our pair interaction drives up the transition temperature. This is true whether the anisotropy favors a configuration in which $\hat{\Omega}_i$ and $\hat{\Omega}_j$ line up with r_{ij}, or a configuration in which $\hat{\Omega}_i$ and $\hat{\Omega}_j$ are orthogonal to r_{ij}. What it says is that, as long as the system is given better instructions on how to pack its molecules, orientational ordering would take place more readily. Second, the effect is not small. Changes as much as 4°K in T_{IN} occur for $w_2(r)$ merely 20% in strength relative to $v_2(r)$. For larger $w_2(r)$ it would not do to apply the present low-order expansion procedure. Numerical alogarithms for solving the integral equation for $g(\mathbf{r} \mid \sigma_2)$ will have to be devel-

TABLE I

Results for $\omega_2 = -9.695$ k°K

$\rho(\text{Å}^{-3})$	T(°K)	σ_2	$F_N - F_I$(k°K/N)
0.002667	404	0.509	−0.855
	405	0.500	−0.302
	405.58	*0.495*	*0.000*
	406	0.490	0.215
	407	0.479	0.728
	408	0.467	1.214
	409	0.455	1.672
0.002670	405	0.506	−0.627
	406	0.497	−0.102
	406.19	*0.495*	*0.000*
	407	0.487	0.425
	408	0.476	0.927
	409	0.463	1.402
	410	0.448	1.848

oped. Third, the order parameter discontinuity at transition *rises* with the inclusion of the w_2 term. This is encouraging. In II, when $v_4(r_{ij})P_4(\hat{\Omega}_i \cdot \hat{\Omega}_j)$ was introduced to reduce the order parameter discontinuity, improvements in several physical quantities emerged. If the same term is introduced into the present model, even more improvement can be expected. Finally, the temperature dependence of σ_2 shows no improvement. It remains too weak.

Table IV shows a number of other properties. We find, unfortunately, that Γ,

TABLE II

Results for $\omega_2 = -19.39$ k°K

$\rho(\text{Å}^{-3})$	T(°K)	σ_2	$F_N - F_I$(k°K/N)
0.002667	404	0.538	−2.754
	405	0.530	−2.127
	406	0.522	−1.521
	407	0.514	−0.934
	408	0.505	−0.370
	408.70	*0.498*	*0.000*
	409	0.495	0.156
0.002670	405	0.535	−2.494
	406	0.527	−1.877
	407	0.518	−1.279
	408	0.510	−0.703
	409	0.501	−0.148
	409.33	*0.498*	*0.000*
	410	0.492	0.295

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TABLE III

Results for $\omega_2 = 19.39$ k°K

$\rho(\text{Å}^{-3})$	T(°K)	σ_2	$F_N - F_I$(k°K/N)
0.002667	404	0.540	−2.860
	405	0.532	−2.227
	406	0.524	−1.615
	407	0.516	−1.024
	408	0.507	−0.454
	408.85	*0.499*	*0.000*
	409	0.498	0.076
0.002670	405	0.537	−2.597
	406	0.528	−1.974
	407	0.520	−1.371
	408	0.512	−0.789
	409	0.503	−0.229
	409.40	*0.499*	*0.000*
	410	0.489	0.372

the slope of $\ln T_{IN} - \ln v$, drops further in magnitude. Other than that, we detect signs of gratifying improvements. To understand the table, we refer the reader to Figure 1, in which v stands for the specific volume $1/\rho$. Now,

$$P_I(v,T) - P_N(v,T) \equiv P_C - P_A = -\left(\frac{\partial(F_I - F_N)}{\partial v}\right)_{v,T,} \tag{36}$$

$$S_I(v,T) - S_N(v,T) \equiv S_C - S_A = -\left(\frac{\partial(F_I - F_N)}{\partial T}\right)_{v,T,} \tag{37}$$

From a Maxwell construction, the fractional volume change is seen to be

$$\frac{\Delta v}{v} \approx K(P_C - P_A), \tag{38}$$

TABLE IV

Physical properties calculated for PAA. Results from II[15] and experiments are included for comparison

ω_2 (k°K)	Γ	$P_C - P_A$(k°K Å^{-3})	$S_C - S_A(k)$	$\frac{\Delta v}{v}$ (%)	ΔH(J/mole)
−19.39	−1.30	0.63	0.51	0.65	2357
−9.690	−1.34	0.61	0.53	0.62	2377
0 (I)	−1.45	0.69	0.52	0.714	2448
+19.39	−1.20	0.65	0.54	0.67	2459
(II)	−1.26			0.46	1452
Experiment	−4.0			0.30–0.36	574–760

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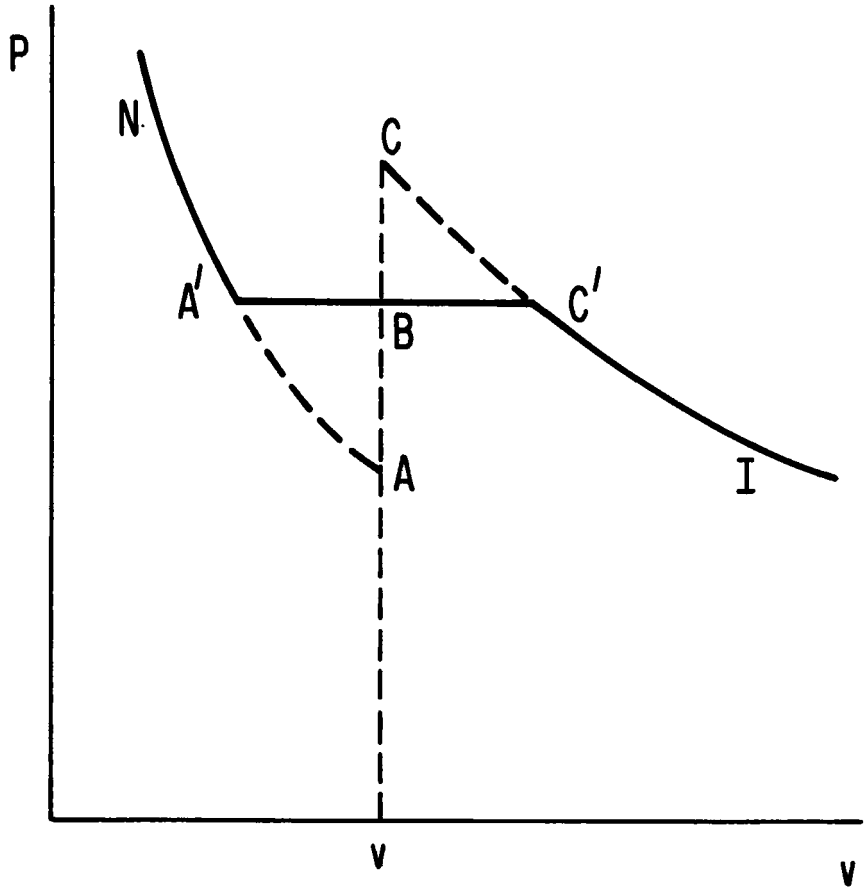

FIGURE 1 Graphic aid for carrying out a Maxwell construction.

where K denotes the isothermal compressibility and is taken to be 7.5×10^{-11} $cm^2/dyne$, as in I. Also, the latent heat is given by

$$\Delta H = T[(S_{C'} - S_C) - (S_{A'} - S_A)] + T(S_C - S_A)$$
$$\approx \left(\frac{\beta T}{K}\right) \Delta v + T(S_C - S_A), \quad (39)$$

where β denotes the coefficient of thermal expansion and is taken to be $7.8 \times 10^{-4}\,{}^\circ K^{-1}$, again as in I.

Note that $(P_C - P_A)$ dropped for all three values of ω_2, —more so for negative ω_2 than positive. This resulted in a healthy improvement in the volume change. $(S_C - S_A)$ changed very little. The improvement in the latent heat for negative ω_2 came mainly from the decrease in Δv.

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We conclude that even in cases of weak anisotropy in the pair interaction, there appear rather significant changes in the predicted physical properties. More work is needed to determine better potential formulas to account for realistic anisotropic interactions and to obtain direction-dependent pair correlation functions.

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