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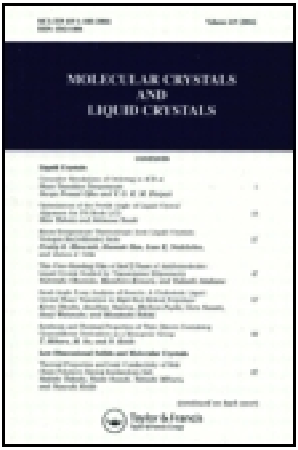

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A Molecular Statistical Theory of Nematic Liquid Crystals (The Effects of a Pair Spatial Correlation Function)

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A Molecular Statistical Theory of Nematic Liquid Crystals

(The Effects of a Pair Spatial Correlation Function)

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The pair spatial correlation function is introduced approximately into mean field theory in terms of an orientation-averaged pair potential, and its effects on nematic–isotropic phase transition are investigated in detail. One finds that the anisotropy of the pairwise intermolecular potential and of the molecular shape account for the stability of nematic order, i.e. increase the long-range orientational order and also the transition temperature. The results of the numerical calculations are compared with experimental data for PAA and with other theoretical results.

1. INTRODUCTION

Maier and Saupe[1] could explain the existence of the first-order nematic–isotropic phase transition by employing a long-range anisotropic dispersion force (London dispersion force[2]), assuming the following orientational pseudo-potential

$$\Phi_1(\theta) = -\frac{A}{V^2}\cdot\langle P_2\rangle\cdot P_2(\cos\theta); \qquad (1.1)$$

here A is a positive constant proportional to the strength of the dispersion force, V is the volume of the system, θ is the angle between the major axis of a molecule and the local director, $P_2(\cos\theta)$ denotes the second Legendre polynomial and $\langle\ \rangle$ represents the ensemble average appropriate to thermal equilibrium. Therefore the order parameter $\langle P_2 \rangle$ is given by

$$\langle P_2 \rangle = \frac{\int_{-1}^{+1} d(\cos\theta) P_2(\cos\theta) e^{-\Phi_1(\theta)/kT}}{\int_{-1}^{+1} d(\cos\theta) e^{-\Phi_1(\theta)/kT}}, \tag{1.2}$$

where k is the Boltzmann constant and T is the absolute temperature. This Eq. (1.2) is a self-consistent equation in the mean field theory. In Maier–Saupe theory (MS theory), however, one cannot account for variation of the transition order parameter $\langle P_2 \rangle_c$ (where c denotes the value at the transition point) and of the transition entropy ΔS with kinds of nematogens.

Some years later, Humphries–James–Luckhurst[3] employed a more general form for the orientational pseudo-potential, adding the fourth Legendre polynomial $P_4(\cos\theta)$, as follows

$$\Phi_1(\theta) = -\frac{A}{V^\gamma}\cdot[\langle P_2 \rangle \cdot P_2(\cos\theta) + \lambda\langle P_4 \rangle \cdot P_4(\cos\theta)]; \tag{1.3}$$

here γ and λ are adjustable parameters determined by comparison with experiments. They could explain variation of $\langle P_2 \rangle_c$ and ΔS by a single parameter λ, and obtained the best agreement with the experimental temperature dependence of the order parameter when γ is equal to four. Cotter pointed out theoretically that γ cannot be treated as an adjustable parameter but must be assigned the value 1.[4] Moreover, taking account of the deviation from spherical symmetry of the pair spatial correlation function of molecules, Humphries *et al.* obtained the orientational pseudo-potential

$$\Phi_1(\theta) = -\frac{A}{V^\gamma}\cdot(1 + \delta\cdot\langle P_2 \rangle)\cdot\langle P_2 \rangle\cdot P_2(\cos\theta), \tag{1.4}$$

where δ denotes the deviation from spherical symmetry of the spatial correlation function.[3] If $\delta = 0$ and $\gamma = 2$, then Eq. (1.4) immediately reduces to Eq. (1.1). We must note here that unless δ is equal to 0, this orientational pseudo-potential is theoretically inconsistent in the sense that the solution of the self-consistent equation does not give minima in the free energy of the system (Gibbs free energy or Helmholtz free energy).

As was mentioned above, the mean field theory of nematic liquid crystals has proved capable of explaining qualitative properties of liquid

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crystals at a molecular level. In this theory, however, pair correlation functions have not been explicitly and consistently taken into account as yet. Comparison of the mean field theory with experimental data and with results of the Monte-Carlo simulations[5] has given rise to a number of questions on the validity of this theory. We shall next mention other theories which include the effects of pair correlations consistently.

Generalized van der Waals theory (GVDW theory),[8-10] which utilizes the scaled particle approach,[6,7] of nematic liquid crystals, has succeeded in explaining many properties of the nematic–isotropic phase transition by taking account of pair correlations arising from hard core repulsions and of the coupling of orientations and positions consistently. In GVDW theory the two body correlation function over which the attractive pair potential is averaged in the internal energy depends not only on the separation of the specified two molecules but also on their orientations. Also the free energy includes a significant contribution from the translational entropy, in addition to the orientational entropy. In this theory, however, the softness of actual nematogens is ignored and therefore the pair excluded volume effect may be overestimated. Furthermore short-range orientational and spatial correlations resulting from intermolecular attractions are completely neglected. The slope of the order parameter $\langle P_2 \rangle$ with temperature is too small to agree with experimental data in this theory.[8]

On the other hand, orientation-averaged pair correlation theory (OAPC theory) proposed by C. W. Woo *et al.*,[11] which is based on the Bogoliubov–Born–Green–Kirkwood–Yvon theory (BBGKY theory), takes account of the pair spatial correlations arising from intermolecular attractions and repulsions; the short-range orientational correlations and the coupling of orientations and positions are neglected as in the mean field theory. This assumption of the decoupling may be somewhat unrealistic in a nematic phase in which the coupling effect contributes to the nematic order. But as far as our interest is directed toward the pair spatial correlations as in this paper, this assumption may be accepted. In OAPC theory the general type of a pairwise intermolecular potential, e.g. Lennared–Jones 6–12 potential, is employed. Therefore one can take account of the softness of molecules. But in Woo's *et al.* theory the anisotropy of the pair spatial correlation function which contributes to nematic order is not considered.

In this paper the focus of interest is a study of the effects of a simplified pair spatial correlation function on nematic–isotropic phase transition. Assuming the decoupling of orientations and positions, we first

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introduce a more general orientation-averaged pair potential than C. W. Woo's *et al.* and approximate the pair spatial correlation function in order to avoid the somewhat difficult process to solve the second BBGKY equation. The approximated pair spatial correlation function is much simpler than C. W. Woo's *et al.*; but involves the deviation from spherical symmetry. Our approach is rather analogous to OAPC theory, rather than GVDW theory and quite concise as shown in next section. Next, we shall compare the numerically calculated results with available experimental data and with the above-mentioned other theoretical results in Section 3. Finally the physical significance and the several shortcomings of the present theory are described in Section 4.

2. THEORY

2.1. Pairwise intermolecular potential

Following the method of Pople,[12] we shall first write down the pairwise intermolecular potential expanded in terms of normalized spherical harmonics Y_{lm} as follows

$$\Phi_{\rm int}(r_{12}, \omega_1, \omega_2) = 4\pi \sum_{l_1 l_2 m} \epsilon_{l_1 l_2;m}(r_{12}) \cdot Y_{l_1 m}(\omega_1) \cdot Y^*_{l_2 m}(\omega_2), \tag{2.1}$$

$$\epsilon_{l_1 l_2;m}(r_{12}) = \frac{1}{4\pi}\int d\omega_1 d\omega_2 \, Y^*_{l_1 m}(\omega_1) \cdot Y_{l_2 m}(\omega_2) \cdot \Phi_{\rm int}(r_{12}, \omega_1, \omega_2). \tag{2.2}$$

Here r_{12} is the distance between the centers of mass of two specified molecules, $\omega_1 = (\theta'_1, \phi'_1)$ and $\omega_2 = (\theta'_2, \phi'_2)$ are the directions of the major axes of molecules with respect to the molecular coordinates as shown in Figure 1, and * represents the conjugate complex. The expansion coefficients $\epsilon_{l_1 l_2;m}(r_{12})$ are found to decrease rapidly with increasing l_1 and l_2.[13] We must note that these two z axes, z_1 and z_2, are in the same direction, which is different from the sense of Pople's notation.[12] $\Phi_{\rm int}$ must be a real quantity and this requires that

$$\epsilon^*_{l_1 l_2;m} = \epsilon_{l_1 l_2;-m}. \tag{2.3}$$

For identical particles the permutation symmetry of $\Phi_{\rm int}$ ensures that

$$\epsilon_{l_1 l_2;m} = (-1)^{l_1+l_2} \epsilon_{l_2 l_1;-m}. \tag{2.4}$$

Provided that the molecule has a space inversion symmetry i.e. employing the following parity relation for spherical harmonics

$$Y_{lm}(\pi - \theta, \pi + \phi) = (-1)^l Y_{lm}(\theta, \phi), \tag{2.5}$$

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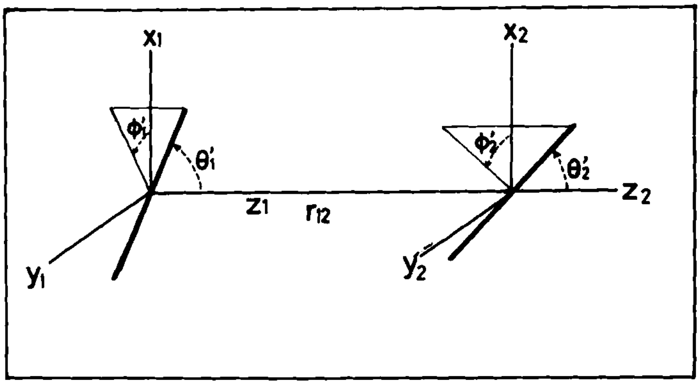

FIGURE 1 Angular coordinate system of two specified interacting molecules.

then only terms with zero and even l_1 and l_2 are required in Eq. (2.1).

Following Humphries-James-Luckhurst,[4] we shall relate the molecular coordinates to the laboratory frame because orientational order in a nematic liquid crystal is defined in terms of molecular orientation with respect to the space-fixed coordinate system. We therefore transform Eq. (2.1) with the aid of the Wigner rotation matrices $D^{l}_{mq}(R)$, i.e.

$$\begin{aligned} Y_{l_1m}(\omega_1) &= \sum_{q_1} Y_{l_1q_1}(\Omega_1)D^{l_1}_{q_1m}(R), \\ Y^{*}_{l_2m}(\omega_2) &= \sum_{q_2} Y^{*}_{l_2q_2}(\Omega_2)D^{l_2*}_{q_2m}(R), \end{aligned} \tag{2.6}$$

where $R = R(\alpha,\beta,\gamma)$ are the Eulerian angles which relate the molecular frame to the laboratory frame, and $\Omega_1 = (\theta_1,\phi_1)$ and $\Omega_2 = (\theta_2,\phi_2)$ are the directions of two specified molecules with respect to the laboratory frame as shown in Figure 2. Substituting Eq. (2.6) into Eq. (2.1), using the following relations with respect to the Wigner rotation matrices,

$$D^{l*}_{qm}(R) = (-1)^{m-q}\cdot D^{l}_{-q-m}(R), \tag{2.7a}$$

$$D^{l_1}_{q_1m}(R)D^{l_2}_{-q_2-m}(R) = \sum_{L=|l_1-l_2|}^{l_1+l_2} C(l_1,l_2,L;m,-m)$$

$$\times\, C(l_1,l_2,L;q_1,-q_2)\cdot D^{L}_{q_1-q_2 0}(R), \tag{2.7b}$$

where $C(l_1,l_2,L;q_1,q_2)$ is the Clebsch–Gordan coefficient,[14] we obtain

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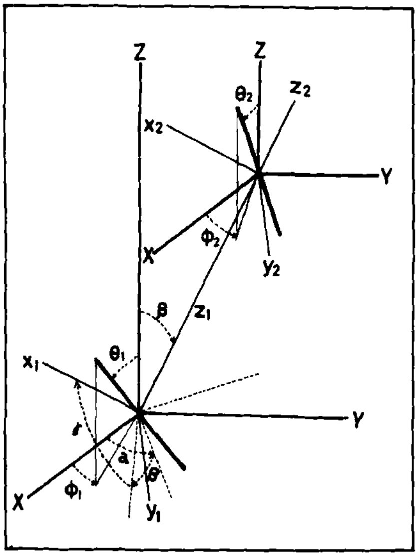

FIGURE 2 Rotation of the coordinates x_1-y_1-z_1: Molecular coordinates of molecule 1. x_2-y_2-z_2: Molecular coordinates of molecule 2. X-Y-Z: Laboratory frame, i.e. space-fixed coordinates.

the pairwise intermolecular potential as a function of r_{12}, $R = R(\alpha,\beta,\gamma)$, Ω_1 and Ω_2 with respect to the laboratory frame, as follows:[4]

$$\Phi_{\text{int}}(r_{12},R,\Omega_1,\Omega_2) = 4\pi \sum_{\substack{l_1 l_2 m \\ q_1 q_2 L}} (-1)^{m-q_2} \cdot C(l_1,l_2,L;m,-m)$$

$$\times\, C(l_1,l_2,L;q_1,-q_2)\,\epsilon_{l_1 l_2;m}(r_{12})\,D^{L}_{q_1-q_2\,0}(R)\,Y_{l_1 q_1}(\Omega_1)\cdot Y^{*}_{l_2 q_2}(\Omega_2). \quad (2.8)$$

We note here that (β,α) denotes the direction of the relative position vector between two specified molecules, 1 and 2.

2.2. Orientation-averaged pair potential

Following C. W. Woo *et al.*,[11] we shall take account of the spatial correlation neglecting the orientational correlation as in the mean field theory. Let us consider a thermal equilibrium system which has volume V and involves N similar particles. It is assumed here that the system is free from any potential of external force and that additivity of the pairwise intermolecular potential holds. In this case, the total potential

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energy of the system is given by

$$\begin{aligned}\Phi_N(Q_1,Q_2,\ldots,Q_N) &= \sum_{i>j}\Phi_{\text{int}}(Q_i,Q_j)\\ &= \sum_{i>j}\Phi_{\text{int}}(r_{ij},\Omega_{ij},\Omega_i,\Omega_j),\end{aligned}\tag{2.9}$$

where $Q_i = (q_i,\Omega_i)$, q_i is the position of the ith molecule's center of mass, Ω_i is the orientational angle of molecule i, and Ω_{ij} denotes the orientation of relative position vector between the centers of mass of molecule i and j with respect to the laboratory frame, e.g. $\Omega_{12} = (\beta,\alpha)$ as $i = 1$ and $j = 2$. (cf. Figure 2) Of course $\Phi_{\text{int}}(r_{12},\Omega_{12},\Omega_1,\Omega_2)$ can be expanded as in Eq. (2.8). We introduce the distribution function for the h molecules in the usual manner

$$\begin{aligned}P^{(h)}_{(Q_1,Q_2,\ldots,Q_h)} &= \left\langle \sum_{i_1,i_2,\ldots,i_h}{}' \delta(Q_1-Q_{i_1})\delta(Q_2-Q_{i_2})\ldots\delta(Q_h-Q_{i_h})\right\rangle\\ &= \frac{N!\displaystyle\int dQ_{h+1}dQ_{h+2}\ldots dQ_N e^{-\Phi_N/kT}}{(N-h)!\displaystyle\int dQ_1dQ_2\ldots dQ_N e^{-\Phi_N/kT}},\end{aligned}\tag{2.10}$$

where the prime on the Σ means that no index in the summation is equal to another, $\langle\ \rangle$ represents the ensemble average as before, and $\delta(Q_n - Q_{i_n})$ $(n = 1,2,\ldots,h)$ is defined as a multiplication of Dirac's δ-function as follows

$$\delta(Q_n - Q_{i_n}) = \delta(q_n - q_{i_n})\,\delta(\cos\theta_n - \cos\theta_{i_n})\,\delta(\phi_n - \phi_{i_n}). \tag{2.11}$$

Employing the distribution function $P^{(N)}$ defined by Eq. (2.10), the internal energy functional due to intermolecular interaction is given by

$$\begin{aligned}&U\{P^{(N)}\}\\ &= U_0 + \frac{1}{N!}\int dQ_1dQ_2\ldots dQ_N P^{(N)}_{(Q_1,\ldots,Q_N)}\Phi_N(Q_1,\ldots,Q_N),\end{aligned}\tag{2.12}$$

where U_0 is the ideal gas internal energy. The entropy functional for the system is given by

$$S\{P^{(N)}\} = S_0 - \frac{k}{N!}\int dQ_1dQ_2\ldots dQ_N P^{(N)}_{(Q_1,\ldots,Q_N)}\log\frac{P^{(N)}_{(Q_1,\ldots,Q_N)}}{N!}, \tag{2.13}$$

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where S_0 is of course the ideal gas entropy. Hence the Helmholtz free energy functional can be constructed as follows

$$F\{P^{(N)}\} = F_0 + \frac{1}{N!}\int dQ_1 dQ_2 \dots dQ_N P^{(N)}_{(Q_1,\dots,Q_N)}\Phi_N(Q_1, \dots, Q_N)$$
$$+ \frac{kT}{N!}\int dQ_1 dQ_2 \dots dQ_N P^{(N)}_{(Q_1,\dots,Q_N)} \log \frac{P^{(N)}_{(Q_1,\dots,Q_N)}}{N!}, \quad (2.14)$$

where F_0 is equal to $U_0 - S_0T$. We are interested in the spatial correlations and therefore neglect the short-range orientational correlations and the coupling of the orientational and spatial correlations as in the mean field theory. Thus we may put

$$P^{(N)}_{(Q_1,Q_2,\dots,Q_N)} = N!\left(\prod_{i=1}^{N} f^{(1)}(\Omega_i)\right)\psi_N(q_1,q_2, \dots, q_N), \quad (2.15)$$

where $f^{(1)}(\Omega_i)$ is the orientational distribution function of the ith molecule, and $\psi_N(q_1,q_2, \dots, q_N)$ represents the spatial correlations. $f^{(1)}(\Omega_i)$ and $\psi_N(q_1,q_2, \dots, q_N)$ obviously satisfy the following condition respectively.

$$\int d\Omega_i f^{(1)}(\Omega_i) = 1, \quad (i = 1,2, \dots, N) \quad (2.16a)$$

$$\int dq_1 dq_2 \dots dq_N \psi_N(q_1,q_2, \dots, q_N) = 1. \quad (2.16b)$$

Next we substitute Eq. (2.14) into Eq. (2.13) and obtain

$$F\{f^{(1)},\psi_N\} = F_0$$
$$+\int dQ_1 \dots dQ_N\left(\prod_{i=1}^{N} f^{(1)}(\Omega_i)\right)\psi_N(q_1, \dots, q_N)\Phi_N(Q_1, \dots, Q_N)$$
$$+ kT\sum_{i=1}^{N}\int d\Omega_i f^{(1)}(\Omega_i)\log f^{(1)}(\Omega_i)$$
$$+ kT\int dq_1 \dots dq_N \psi_N(q_1, \dots, q_N)\log \psi_N(q_1, \dots, q_N). \quad (2.17)$$

In OAPC theory $f^{(1)}(\Omega_i)$ $(i = 1,2, \dots, N)$ and $\psi_N(q_1,q_2, \dots, q_N)$ are to be determined by minimizing the free energy functional (2.17) under the constraints (2.16a) and (2.16b).[11] But this approach requires

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a somewhat difficult process, i.e. one requires the solution of the second BBGKY equation,[11]

$$\frac{\partial}{\partial q_1} \log \tilde{g}^{(2)}(q_{12};\langle P_l\rangle, V, T) = -\frac{1}{kT}\cdot\frac{\partial}{\partial q_1}\,\bar{\Phi}_{\text{int}}(q_{12};\langle P_l\rangle)$$

$$-\frac{N}{VkT}\int dq_3\left[\frac{\partial}{\partial q_1}\,\bar{\Phi}_{\text{int}}(q_{13};\langle P_l\rangle)\right]\frac{\tilde{g}^{(3)}(q_{12},q_{23},q_{31};\langle P_l\rangle,V,T)}{\tilde{g}^{(2)}(q_{12};\langle P_l\rangle,V,T)}, \quad (2.18)$$

where $\tilde{g}^{(2)}$ and $\tilde{g}^{(2)}$ are the spatial correlation function for the two and three bodies respectively, and $\bar{\Phi}_{\text{int}}$ is the orientation-averaged pair potential. $q_{12} = (r_{12}, \Omega_{12})$, where $\Omega_{12} = (\beta,\alpha)$ describes the orientation of the center of mass separation vector with respect to the space-fixed frame. The explicit form of this potential will be below. Using the Kirkwood's superposition approximation for $\tilde{g}^{(3)}$, C. W. Woo *et al.*[11] solved the second BBGKY Eq. (2.18). They did not take account of the anisotropy of the pair spatial correlation function and therefore the solution of Eq. (2.18) depended only on the separation of the specified two molecules. But the process to solve the Eq. (2.18) is somewhat difficult when the anisotropy of the pair spatial correlation function is concerned. In contrast to their approach, we shall now introduce a simplified pair spatial correlation function which involves the deviation from spherical symmetry. From Eq. (2.18) we approximate the trial pair spatial correlation function at short range as follows

$$\tilde{g}^{(2)}(q_{12};\langle P_l\rangle,T) = e^{-\bar{\Phi}_{\text{int}}(q_{12};\langle P_l\rangle)/kT} \quad (2.19)$$

This trial pair spatial correlation function corresponds to the expression which retains the first term of the rhs of Eq. (2.18). Although this approximation is valid only in a dilute gas system and unrealistic for a high density system such as liquid crystals, the temperature dependence of the pair spatial correlation function approximated as Eq. (2.19) is more reasonable than that of the mean field theory, in which one neglects the temperature dependence of the pair spatial correlation function in order to retain the consistency of the theory.[4] This simplification, of course, may be drastic; but the qualitative properties of the pair spatial correlation function at short range will be retained. In addition to this approximation we neglect the contribution of the translational entropy to the Helmholtz free energy as a first approximation, as in the mean field theory. According to the above approximations, we put forward the following simplified Helmholtz free energy functional in-

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stead of Eq. (2.17), employing the trial pair spatial correlation function in Eq. (2.19),

$$F\{f^{(1)}\} = \frac{N}{2}\cdot\frac{N}{V}\cdot\int dq_{12}\,\tilde{\Phi}_{\text{int}}(q_{12};\langle P_l\rangle)\tilde{g}^{(2)}(q_{12};\langle P_l\rangle,T)$$

$$+ NkT\int d\Omega_1 f^{(1)}(\Omega_1)\log f^{(1)}(\Omega_1) + \text{independent of } f^{(1)}(\Omega_1). \quad (2.20)$$

Here

$$\tilde{\Phi}_{\text{int}}(q_{12};\langle P_l\rangle) = \int d\Omega_1 d\Omega_2 f^{(1)}(\Omega_1)f^{(1)}(\Omega_2)\,\Phi_{\text{int}}(q_{12},\Omega_1,\Omega_2). \quad (2.20\text{a})$$

The first term in Eq. (2.20) involves the orientation-averaged pair potential $\tilde{\Phi}_{\text{int}}$ which results from an orientational average of the full two body interaction Φ_{int}; the internal energy is an average of $\tilde{\Phi}_{\text{int}}$ over its corresponding spatial correlation function $\tilde{g}^{(2)}$, approximated by $\exp(-\tilde{\Phi}_{\text{int}}/kT)$. The second term in Eq. (2.20) is an "entropy of mixing", or "orientational entropy". That is, the theory neglects all "translational" (or "packing") entropy contribution. The present theory is defined completely by Eq. (2.20) for the Helmholtz free energy functional and by the accompanying relations in Eq. (2.19) for $\tilde{g}^{(2)}$ and Eq. (2.20a) for $\tilde{\Phi}_{\text{int}}$.

Here from Eq. (2.8) the orientation-averaged pair potential $\tilde{\Phi}_{\text{int}}(q_{12};\langle P_l\rangle)$ is, in more general form than one of Ref. 11, given by

$$\tilde{\Phi}_{\text{int}}(q_{12};\langle P_l\rangle) = \sum_{Ll_1l_2} \epsilon^{L}_{l_1l_2}(r_{12})\cdot D^{L}_{00}(R)\cdot\langle P_{l_1}\rangle\cdot\langle P_{l_2}\rangle, \quad (2.21)$$

where $\epsilon^{L}_{l_1l_2}(r_{12})$ is defined as follows

$$\epsilon^{L}_{l_1l_2}(r_{12}) = \sum_{m} (-1)^m C(l_1,l_2,L;m,-m)C(l_1,l_2,L;0,0)$$

$$\times(2l_1+1)^{1/2}\cdot(2l_2+1)^{1/2}\cdot\epsilon_{l_1l_2;m}(r_{12}). \quad (2.22)$$

We must note here that the terms corresponding to $l_1 \neq l_2$ result in anisotropic steric effects. Provided that $L = 0$ and $l_1 = l_2 = 0,2,4$, this orientation-averaged potential reduces to which C. W. Woo *et al.* used.[11] In addition the symmetry of the Clebsch–Gordan coefficients[14]

$$C(l_1,l_2,L;m_1,m_2) = C(l_2,l_1,L;-m_2,-m_1)$$

$$= (-1)^{l_1+l_2-L}C(l_1,l_2,L;-m_1,-m_2), \quad (2.23)$$

together with Eqs. (2.3) and (2.4), yields the symmetry of the coefficient $\epsilon^{L}_{l_1l_2}(r_{12})$

$$\epsilon^{L}_{l_1l_2}(r_{12}) = (-1)^{l_1+l_2}\epsilon^{L}_{l_2l_1}(r_{12}) = (-1)^{l_1+l_2-L}\epsilon^{L}_{l_1l_2}(r_{12}). \quad (2.24)$$

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In Eq. (2.21) the order parameters $\langle P_l \rangle$ is defined by

$$\langle P_l \rangle = \int d\Omega f^{(1)}(\Omega) \cdot P_l(\cos\,\theta). \tag{2.25}$$

Since the pair spatial correlation function has a space inversion symmetry in nematic liquid crystals, the possible value of L is reduced to zero and even.

Now we take the functional derivative of Eq. (2.20) with respect to $f^{(1)}(\Omega)$, under the constraints shown in Eq. (2.16a), and readily obtain

$$f^{(1)}(\theta_1) = \frac{e^{-\Phi_1(\theta_1)/kT}}{Z_1} = \frac{1}{2\pi} \sum_l \frac{2l+1}{2} \langle P_l \rangle \cdot P_l(\cos\,\theta_1), \tag{2.26}$$

$$\Phi_1(\theta_1) = \frac{N}{V} \int dq_{12} d\Omega_2 f^{(1)}(\Omega_2) g^{(2)}(q_{12}; \langle P_l \rangle, T)\, \Phi_{\text{int}}(q_{12}, \Omega_1, \Omega_2), \tag{2.27}$$

$$Z_1 = \int d\Omega_1 e^{-\Phi_1(\theta_1)/kT}, \tag{2.28}$$

$$\mathring{g}^{(2)}(q_{12}; \langle P_l \rangle, T) = \left(1 - \frac{\bar{\Phi}_{\text{int}}(q_{12}; \langle P_l \rangle)}{kT} \right) e^{-\Phi_{\text{int}}(q_{12}; \langle P_l \rangle)/kT}, \tag{2.29}$$

where $\Phi_1(\theta_1)$ is the orientational pseudo-potential for the molecule 1, Z_1 is the one body partition function, and $\mathring{g}^{(2)}(q_{12}; \langle P_l \rangle, T)$ is the modified pair correlation function which ensures the consistency of our theory. From Eqs. (2.8) and (2.21), together with Eq. (2.25), one obtains the following set of self-consistent equations.

$$\langle P_l \rangle = \frac{\int d\Omega_1 P_l(\cos\,\theta_1) e^{-\Phi_1(\theta_1)/kT}}{\int d\Omega_1 e^{-\Phi_1(\theta_1)/kT}}, \tag{2.30}$$

$$\Phi_1(\theta_1) = \sum_{l_1 l_2} u_{l_1 l_2}(\langle P_l \rangle, V, T) \cdot P_{l_1}(\cos\,\theta_1) \cdot \langle P_{l_2} \rangle, \tag{2.31}$$

$$u_{l_1 l_2}(\langle P_l \rangle, V, T) = 2\pi \cdot \frac{N}{V} \sum_L \int_0^\infty r_{12}^2 dr_{12}\, \epsilon_{l_1 l_2}^L(r_{12}) g_L(r_{12}; \langle P_l \rangle, T), \tag{2.32}$$

$$g_L(r_{12}; \langle P_l \rangle, T) = \int_{-1}^{+1} d(\cos\,\theta_{12}) P_L(\cos\,\theta_{12}) \mathring{g}^{(2)}(q_{12}; \langle P_l \rangle, T). \tag{2.33}$$

From Eq. (2.20) the entropy functional is given by

$$S\{f^{(1)}\} = -\left(\frac{\partial F\{f^{(1)}\}}{\partial T} \right)_{V f^{(1)}} = -Nk \int d\Omega_1 f^{(1)}(\Omega_1) \log f^{(1)}(\Omega_1)$$

$$- \frac{N}{2} \cdot \frac{N}{V} \cdot k \int dq_{12} \left(\frac{\bar{\Phi}_{\text{int}}}{kT} \right)^2 e^{-\bar{\Phi}_{\text{int}}/kT}. \tag{2.34}$$

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Therefore the internal energy functional is readily derived as follows

$$U\{f^{(1)}\} = F\{f^{(1)}\} + S\{f^{(1)}\}\cdot T$$

$$= \frac{N}{2}\cdot\frac{N}{V}\cdot\int dq_{12}\,\bar{\Phi}_{\mathrm{int}}\mathring{g}^{(2)}(q_{12};\langle P_l\rangle,T). \qquad (2.35)$$

The excess specific heat at constant volume C_V is calculated as follows

$$C_V = \left(\frac{\partial U\{f^{(1)}\}}{\partial T}\right)_V. \qquad (2.36)$$

Using the modified pair spatial correlation function, one can calculate the number of the nearest neighbor molecules z as follows

$$z = \frac{N}{V}\int_{\mathrm{cell}} dq_{12}\mathring{g}^{(2)}(q_{12};\langle P_l\rangle,T), \qquad (2.37)$$

where "cell" on the integral sign means that the volume integral range is restricted to within a virtual cell which includes nearest neighbors but excludes next-nearest neighbors or more. The number z is the effective number of molecules interacting with the center molecule.

2.3. Approximations

For the practical calculations, we introduce the model potential, Lennard–Jones 6–12 type, and retain the following coefficients of the orientation-averaged pair potential in Eq. (2.21), and set others equal to 0;

$$\epsilon_{00}^{0}(r_{12}) = \epsilon_{00;0}(r_{12}) \equiv U_{00}^{0}\left\{\left(\frac{r_0}{r_{12}}\right)^{12} - 2\cdot\left(\frac{r_0}{r_{12}}\right)^{6}\right\},$$

$$\epsilon_{22}^{0}(r_{12}) = 5\sum_{m}(-1)^m C(2,2,0;m,-m)\,C(2,2,0;0,0)\,\epsilon_{22};m(r_{12})$$

$$\equiv U_{22}^{0}\left\{\left(\frac{r_0}{r_{12}}\right)^{12} - 2\cdot\left(\frac{r_0}{r_{12}}\right)^{6}\right\},$$

$$\epsilon_{02}^{2}(r_{12}) = \epsilon_{20}^{2}(r_{12}) = \epsilon_{20;0}(r_{12})$$

$$\equiv U_{02}^{2}\left\{\left(\frac{r_0}{r_{12}}\right)^{12} - 2\cdot\left(\frac{r_0}{r_{12}}\right)^{6}\right\}$$

$$\epsilon_{44}^{0}(r_{12}) = 9\sum_{m}(-1)^m C(4,4,0;m,-m)\,C(4,4,0;0,0)\,\epsilon_{44};m(r_{12})$$

$$\equiv -2U_{44}^{0}\left(\frac{r_0}{r_{12}}\right)^{6}. \qquad (2.38)$$

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Here the equality $\epsilon^2_{02} = \epsilon^2_{20}$ is due to Eq. (2.24). We shall note the physical meanings of these coefficients: ϵ^0_{00} is the spherical component of the pairwise intermolecular potential; and ϵ^0_{22} is the anisotropic component which plays a dominant role for the nematic order as shown later. ϵ^2_{20} is the anisotropic component which gives rise to the deviation from spherical symmetry of the pair spatial correlation function and reflects the anisotropy of the molecular shape, i.e. $U^2_{20} < 0$ corresponds to a rod-like molecule and $U^2_{20} > 0$ corresponds to a disk-like one.[12] ϵ^0_{44} represents the contribution from the higher order intermolecular interactions. Taking account of the report with respect to the energetical computation of pairwise intermolecular potential for PAA by Jan Baran *et al.*,[15] we set r_0 equal to 5.5 (Å). For convenience we introduced the reduced temperature T^* and the reduced number density ρ^* $(\rho = N/V)$

$$T^* = kT/U^0_{22}, \quad \rho^* = \rho/\rho_0,$$

and the parameters σ, μ, and ν as follows.

$$\sigma = U^0_{00}/U^0_{22}, \quad \mu = U^0_{44}/U^0_{22}, \quad \nu = U^2_{02}/U^0_{22};$$

here we chose the average number density ρ_0 equal to 2.667×10^{21} (l/cm^3) for PAA at 408 (K) and 1 (bar).[1]

We give the value of the parameters, σ, μ, and ν as data and calculate the temperature dependence (T^* dependence) of the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ at constant volume, using the set of self-consistent equations, (2.21) and (2.30–2.33). Here we assumed that the radius of the cell in Eq. (2.37) is equal to 7.5 (Å).

3. RESULTS

We shall show the results of numerical calculations in this section. We first investigate the effects caused by the parameters σ, μ, and ν respectively.

First we show, in Figure 3 and Table I, the effects of the parameter σ in the case $\mu = \nu = 0$. In Table I z_N and z_I represent the number of nearest neighbors calculated from Eq. (2.36) in the nematic and isotropic phase, respectively at the transition point. In this case the pair spatial correlation function has spherical symmetry and therefore $u_{l_1 l_2}$ is equal to 0 unless $l_1 = l_2$ [cf. Eqs. (2.29), (2.32), and (2.33)] As the anisotropic component ϵ^0_{22} increases, i.e. the parameter σ decreases, the transition order parameters $\langle P_2 \rangle_c$ and $\langle P_4 \rangle_c$ (where c denotes the value at the transition point as before) and also the transition entropy $\Delta S/N.k$ in-

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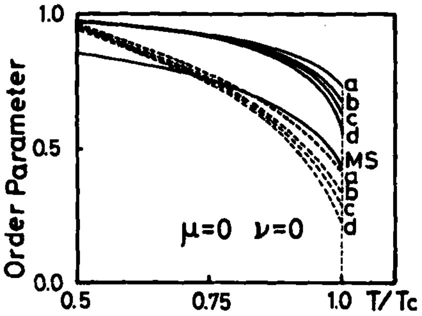

FIGURE 3 The dependence of order parameters on the parameter σ. (a) $\sigma = 1.0$, (b) $\sigma = 2.0$, (c) $\sigma = 3.0$, (d) $\sigma = 7.0$; here $\mu = \nu = 0$.

crease, whereas the reduced transition temperature T_c^* decreases. We must note here that the actual transition temperature $T_c = U_{00}^0/(\sigma.k)T_c^*$ increases provided that the spherical component U_{00}^0 are approximately constant. This result may be expected for an actual homologous series, e.g. PAA, PAP, DPAB and so on. From Figure 3 the calculated order parameter in the case $\mu = 0$ is found to be higher than one of MS theory or experimental data at constant volume.[16] Therefore we must take account of the parameter μ, which causes the decrease of nematic order and also transition entropy when $\mu < 0$. The results are shown in Figure 4. This kind of effect was first investigated by Humphries-James-Luckhurst in the mean field theory, as was mentioned in Section 1. Since $\mu < 0$, u_{44} in Eq. (2.31) is positive; this results in the reduction of the depth of the orientational pseudo-potential shown in Eq. (2.31) about $\theta = 0$. Consequently the increase of $|\mu|$ ($\mu < 0$) causes the decrease of nematic order. We summarize the above results in Table II.

Next we shall show, in Figure 5, the effects of the parameter ν which causes the deviation from spherical symmetry of the pair spatial correlation function. As was mentioned before, $\nu < 0$ corresponds to a rod-like molecule and $\nu > 0$ corresponds to a disk-like one. In both cases the order parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$, and also the reduced transition

TABLE I

The effects of the parameter σ.

$\nu=\mu=0.0$						
σ	T_c^*	$\langle P_2\rangle_c$	$\langle P_4\rangle_c$	Z_N	Z_I	$\Delta S/Nk$
1.0	1.514	0.736	0.394	11.2	7.59	2.54
2.0	2.040	0.675	0.318	13.7	10.8	2.36
3.0	2.513	0.637	0.278	16.2	13.6	2.27
7.0	4.161	0.551	0.201	24.7	22.9	2.00

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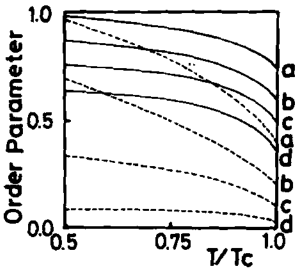

FIGURE 4 The dependence of order parameters on the parameter μ. (a) $\mu = 0.0$, (b) $\mu = -0.2$, (c) $\mu = -0.5$, (d) $\mu = -2.0$; here $\sigma = 1.0$ and $\nu = 0$.

temperature T_c^* increases when $|\nu|$ increases. This result suggests that the anisotropic steric effects contribute to nematic order.

Finally we shall compare our theoretical results with available experimental data and determine the unknown parameters σ and μ so that the theoretical curve for the order parameter $\langle P_2 \rangle$ at constant volume fits the experimental one.[16] But we cannot determine the parameter ν because we have no available experimental data of the fourth order parameter $\langle P_4 \rangle$ for PAA to determine this one. Provided that the experimental data of $\langle P_4 \rangle$ for PAA at constant volume is obtained, this parameter may be determined as shown in next section. Therefore at this stage we put $\nu = 0$. We first determine σ in order to fit the slope of the theoretical curve for $\langle P_2 \rangle$ to experimental one. We then determine the other parameter μ in order to adjust the transition value of order parameter $\langle P_2 \rangle_c$ to the experimental value. According to the above procedures, we have the parameters σ and μ

$$\sigma = 2.0, \quad \mu = -1.0 \quad (T_c^* = 1.946)$$

respectively for PAA. In other words, the anisotropic component of the intermolecular potential is half as large as the spherical component

TABLE II

The effects of the parameter μ.

$\sigma=1.0$ $\nu=0.0$						
μ	T_c^*	$\langle P_2 \rangle_c$	$\langle P_4 \rangle_c$	Z_N	Z_I	$\Delta S/Nk$
0.0	1.514	0.736	0.394	11.2	7.59	2.54
-0.1	1.477	0.650	0.271	10.5	7.73	1.87
-0.2	1.455	0.584	0.196	10.0	7.82	1.48
-0.5	1.423	0.473	0.098	9.38	7.95	0.957
-0.7	1.413	0.434	0.072	9.20	8.00	0.805
-1.0	1.404	0.397	0.050	9.05	8.04	0.676
-2.0	1.391	0.344	0.025	8.87	8.10	0.511

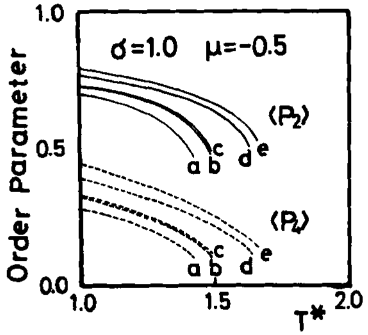

FIGURE 5 The dependence of order parameters on the parameter ν. (a) $\nu = 0.0$, (b) $\nu = -0.5$, (c) $\nu = 0.5$, (d) $\nu = -1.0$, (e) $\nu = 1.0$; here $\sigma = 1.0$ and $\mu = -0.5$.

and also is nearly equal to the component due to the higher order interactions apart from their signs.

We show the results in Figure 6, together with the results of GVDW theory,[8] OAPC theory, and MS theory for comparison. One can find that the present theoretical curve attains the good agreement with the experimental data near the transition point and also its profile is closer to OAPC's one.

The excess specific heat at constant volume C_V is calculated from Eq. (2.36) and shown in Figure 7. The value of C_V in nematic phase is greater than one of the Pople–Karasz theory[17] by about a factor of 20; but smaller than the experimental value,[17] by about a factor of 2.

We show the temperature dependence of the number of nearest neighbors in Figure 8. From this result we may predict that the number of nearest neighbors changes from about 12 to 11 on nematic–isotropic phase transition for PAA.

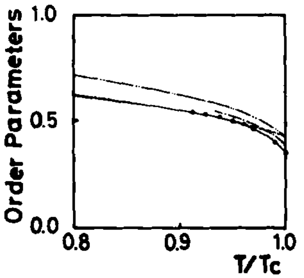

FIGURE 6 Comparison with experimental data and other theoretical results. Open circles represent the experimental second order parameter measured by J. R. McColl and C. S. Shih.[16] ——— for the present theory ($\sigma = 2$, $\mu = -1$, and $\nu = 0$); ---- for GVDW theory;[8] —·—·— for OAPC theory;[11] —··—··— for MS theory.

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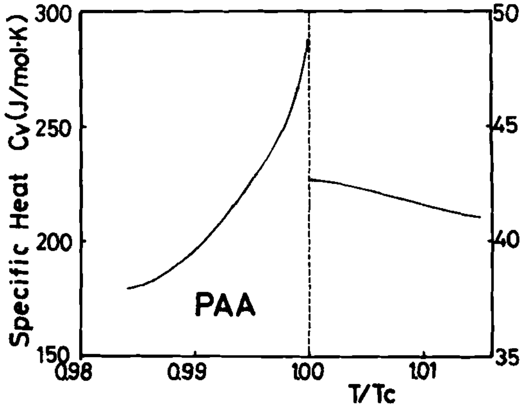

FIGURE 7 The excess specific heat at constant volume, where $\sigma = 2$, $\mu = -1$, and $\nu = 0$.

Finally we show the density dependence of the order parameters in Figure 9. One finds that $\langle P_2 \rangle_c$ and $\langle P_4 \rangle_c$ are constant with respect to the change of the reduced number density ρ^*. This result is consistent with the experimental findings.[16] As far as log T^* − log ρ^* plot at constant $\langle P_2 \rangle$ is concerned, we obtained the straight lines as shown in Figure 10. But the slopes of these lines are too small (0.4 ~ 0.5) and quite far from the experimental value 4.0 ± 0.1 for PAA.[16] In addition we took account of the effect of the parameter ν, i.e. anisotropic steric effects; but the agreement was not as good as the case $\nu = 0$, in contrast to the discussion by C. W. Woo *et al.*[11]

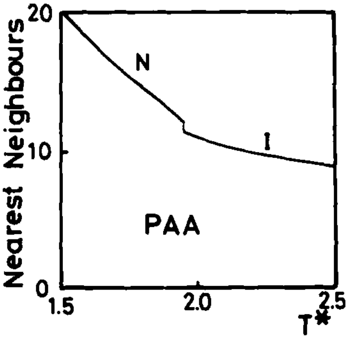

FIGURE 8 The number of nearest neighbor molecules for PAA, where $\sigma = 2$, $\mu = -1$, and $\nu = 0$.

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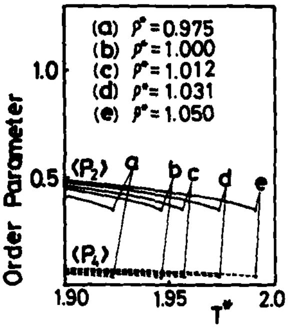

FIGURE 9 The dependence of order parameters on the number density, where $\sigma = 2$, $\mu = -1$, and $\nu = 0$.

4. DISCUSSIONS

We shall mention the significance and the several shortcomings of the present theory in this section. Our interests are directed toward the property of the effective pair potential $u_{l_1 l_2}$ in the self-consistent equations for the order parameters, $\langle P_2\rangle$ and $\langle P_4\rangle$,

$$\langle P_2\rangle = \frac{\displaystyle\int_{-1}^{+1} d(\cos\,\theta_1) P_2(\cos\,\theta_1) e^{-[(u_{20}+u_{22}\langle P_2\rangle)P_2(\cos\theta_1)+u_{44}\langle P_4\rangle P_4(\cos\theta_1)]/kT}}{\displaystyle\int_{-1}^{+1} d(\cos\,\theta_1) e^{-[(u_{20}+u_{22}\langle P_2\rangle)P_2(\cos\theta_1)+u_{44}\langle P_4\rangle P_4(\cos\theta_1)]/kT}}, \quad (4.1)$$

$$\langle P_4\rangle = \frac{\displaystyle\int_{-1}^{+1} d(\cos\,\theta_1) P_4(\cos\,\theta_1) e^{-[(u_{20}+u_{22}\langle P_2\rangle)P_2(\cos\theta_1)+u_{44}\langle P_4\rangle P_4(\cos\theta_1)]/kT}}{\displaystyle\int_{-1}^{+1} d(\cos\,\theta_1) e^{-[(u_{20}+u_{22}\langle P_2\rangle)P_2(\cos\theta_1)+u_{44}\langle P_4\rangle P_4(\cos\theta_1)]/kT}}.$$

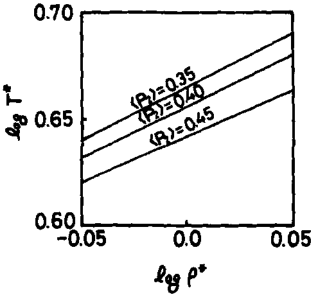

FIGURE 10 The plots of log ρ^* — log T^* at constant order parameter, where $\sigma = 2$, $\mu = -1$, $\nu = 0$.

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Provided that $\langle P_2\rangle = 0$, one finds that $u_{20} = u_{02} = 0$ from Eqs. (2.21), (2.29), (2.32), and (2.33). Therefore the solution $\langle P_2\rangle = \langle P_4\rangle = 0$, which corresponds to isotropic liquid phase, is one of the solutions through the all temperature range.

Now assuming $u_{20} = u_{02} = u_{44} = 0$, we compare the temperature dependence of the order parameter in the present theory with some other theoretical results. The self-consistent equation, which determines the temperature dependence of the order parameter, may be written in general as follows,

$$\langle P_2\rangle = \frac{\int_{-1}^{+1} d(\cos\theta) P_2(\cos\theta) e^{-[\Lambda(V,T)/kT]\langle P_2\rangle P_2(\cos\theta)}}{\int_{-1}^{+1} d(\cos\theta) e^{-[\Lambda(V,T)/kT]\langle P_2\rangle P_2(\cos\theta)}}; \qquad (4.2)$$

Here the coefficient $\Lambda(V,T)$, which just corresponds to u_{22} in the present theory, is a function of the volume and temperature, and involves intermolecular attractions and repulsions in GVDW theory,[8] OAPC theory,[11] and our theory; but in MS theory it involves only the attractions and corresponds to $-A/V^2$ in Eq. (1.1). In MS theory and GVDW theory

$$\left(\frac{\partial\Lambda}{\partial T}\right)_V = 0, \quad \left(\frac{\partial\Lambda}{\partial T}\right)_V < 0$$

respectively, whereas in the present theory

$$\left(\frac{\partial\Lambda}{\partial T}\right)_V > 0.$$

It seems that these differences result in variations of the order parameter change as shown in Figure 6. The slope of the curves for $\langle P_2\rangle$ near the transition point is found to be most abrupt in the present theory and also in OAPC theory. One may deduce that this abrupt change in the present theory is mainly due to the temperature dependence of $\Lambda(V,T)$ (or u_{22}) because the slope of $\langle P_2\rangle$ curve near the transition point is not critically affected by u_{44} as expected from Figure 4. Since $(\partial\Lambda/\partial T)_V > 0$, the long-range orientational order parameter decreases abruptly when temperature increases. Hence the temperature dependence of the coefficient $\Lambda(V,T)$, i.e. of the pair spatial correlation function is significant so as to explain the abrupt decrease of the order parameter near a transition point as found in some experiments.[18] One may infer that the discrepancy in GVDW theory as shown in Figure 6 is mainly due to the disregard of the softness of actual molecules as we have noted in Section 1.

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We can determine the parameters of our model potential, U_{00}^{0}, U_{22}^{0} and U_{44}^{0}, using the experimental transition temperature at constant volume for PAA, 437.5 (K),[16] together with $\sigma = 2$ and $\mu = -1$ (which were determined in the previous section) and obtain

$$U_{00}^{0} = 450 \text{ K}, \quad U_{22}^{0} = -U_{44}^{0} = 225 \text{ K}.$$

Our theoretical transition entropy $\Delta S/N.k$ for PAA is equal to 0.632 and smaller than one of GVDW theory, 0.887;[8] but much greater than the experimental value, 0.19.[19] It seems that this discrepancy between our theoretical results and the experimental data is due to the disregards of the short-range orientational correlations and of biaxiality in the molecular symmetry,[20] in addition to the drastic approximation shown in Eq. (2.19). But our theoretical results reflect qualitatively the effects of the pair spatial correlation function.

Finally we shall mention the possibility to determine the parameter ν. In Figure 11, we show the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ where the former order parameters are fitted to the experimental data for PAA in terms of the aforementioned manner. The parameters ν for the curves *a* and *b* are 0 and -1 respectively, where we assumed that the parameter σ is constant in both cases. As far as the second order parameter $\langle P_2 \rangle$ is concerned, the set of the parameters, σ, μ, and ν cannot be uniquely determined. However, provided that one obtains the experimental data of the fourth order parameter $\langle P_4 \rangle$ in addition to $\langle P_2 \rangle$ at constant volume, it seems possible to determine the all parameters, σ, μ, and ν, uniquely. Unfortunately, there is no data of $\langle P_4 \rangle$ at constant volume for PAA as far as we know. Although, strictly speaking, it is not correct to compare directly the present theoretical order parameter $\langle P_4 \rangle$ at constant volume with the experimental one at constant pressure, we show the temperature dependence of the ratio $\langle P_4 \rangle / \langle P_2 \rangle$ derived from the present theory and the experiment[21] in Figure 12 for comparison. It is found that the temperature dependence of them is not quantitatively but qualitatively in agreement.

5. CONCLUSION

We introduced approximately the pair spatial correlation function into the mean field theory in terms of the orientation-averaged pair potential and investigated the effects of the anisotropy of the pairwise intermolecular potential and the effects of the pair spatial correlation func-

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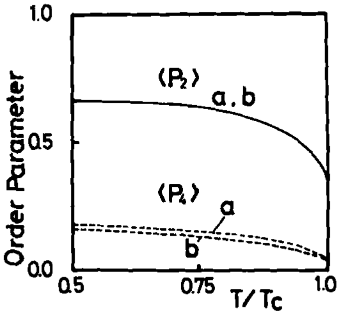

FIGURE 11 The theoretical curves for $\langle P_2 \rangle$ and $\langle P_4 \rangle$ are shown, where the sets of parameters for curves *a* and *b* are given as follows. (a) $\sigma = 2$, $\mu = -1$, and $\nu = 0$. ($T_c^* = 1.946$) (b) $\sigma = 2$, $\mu = -1.5$, and $\nu = -1$. ($T_c^* = 2.122$) The curves for $\langle P_2 \rangle$ of the two sets are fitted to the experimental data for PAA.[16] The two sets of parameters give nearly the same curve for $\langle P_2 \rangle$, but different curves for $\langle P_4 \rangle$.

tion on nematic–isotropic phase transition. From the numerically calculated results, we found that the anisotropy of a pairwise intermolecular potential increases both the long-range orientational order and the nematic–isotropic transition temperature. The calculated order parameter change near the transition point was in good agreement with the experimental data for PAA, but the agreement with respect to the specific heat at constant volume and the transition entropy was not good, probably because of the disregards of the short-range orientational correlations and of the coupling of orientational and spatial correlations.

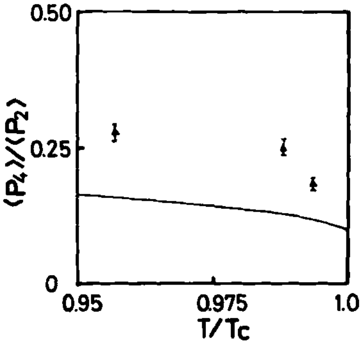

FIGURE 12 The comparison of $\langle P_4 \rangle / \langle P_2 \rangle$. The solid line is for the present theoretical results at constant volume ($\sigma = 2$, $\mu = -1$, $\nu = 0$). The triangular symbols are for the experimental data at constant pressure by M. Kohli *et al.*[21]

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