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Orientational Phase Transition of Long Elongated Gay–Berne Molecules

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We have performed a detailed study of the temperature dependence and of the isotropic–nematic phase transition in a fluid of moderately long elongated molecules interacting via a Gay–Berne potential with anisotropy parameters $x_0 = 4.4, k' = 20.0, \mu = 1, and\ \nu = 1$. *The nematic phase is found to be stable with respect to the isotropic phase for reduced temperatures* $T^* \leq 1.60$. *In the temperature range* $1.60 \leq T^* \leq 3.0$, *the phase boundaries of the isotropic–nematic transition are obtained by using the density-functional theory. The pair-correlation functions of the isotropic phase that enter in the density-functional theory as input informations are found from the Percus–Yevick integral equation theory. The accuracy of the Percus–Yevick integral equation theory has been tested by comparing the pair-correlation functions of the Gay–Berne fluids with computer simulation results. The density-functional theory is good enough to study the freezing parameters of complex fluids if the values of the pair-correlation functions of the isotropic phase are known accurately.*

Keywords: density-functional theory; Gay–Berne potential; isotropic–nematic transition; pair-correlation functions

1. INTRODUCTION

A number of computationally efficient pair-interaction models have been proposed over the past decades for the study of liquid-crystalline mesogens [1]. In particular, fluids composed of elongated (prolate) molecules constitute an important class of liquid crystals with relevant industrial and biological applications. Most commonly used models are hard ellipsoids of revolution, hard spherocylinders [2,3], cut sphere, the Kihara core model [4,5], and the Gay–Berne [6] model.

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All these are single-site models and refer to rigid molecules of cylindrical symmetry. Even for these simple models, calculating the complete phase diagram is difficult.

Hard anisometric molecules have been found to yield a variety of liquid-crystalline phases as the density is varied [7]. In addition, the particular shape of the molecules has also been found to play an essential role in the phase behavior. For example, hard prolate ellipsoids have been shown to exhibit a nematic phase but do not yield smectic phases [8]. For these translationally ordered phases to be formed from ellipsoidal molecules, it is necessary to introduce anisotropic attractive forces into the potential model; this has the added benefit that the phase transitions are now thermally driven [9]. Shape anisotropy and the attractive forces, which always exist between real molecules, are the two major factors responsible for the existence of liquid crystals. One of the potentials fulfilling this condition and being remarkably successful for the computer modeling of liquid-crystalline molecules is the single-site, anisotropic pair potential of Lennard–Jones type, developed by Gay and Berne [6].

Computer simulation studies of systems composed of prolate molecules interacting via a Gay–Berne (GB) potential have revealed a rich phase behavior. In a wide range of reported simulation studies, various forms of the GB model have been shown to exhibit stable isotropic, nematic, smectic A, and smectic B mesophases [10–14] and a number of alternative parameterizations have been investigated [10,15–19]. Some theoretical attempts have also been made to calculate the GB phase diagram using density-functional approach, perturbation methods, and virial approximations [20–23]. It is now clear that a large number of computer simulation studies have been made to find the complete phase diagram of the GB fluid; however, to our knowledge, not much theoretical investigation of the liquid-crystalline phase diagram of the GB systems has been made.

The work presented here concentrates on the location of the isotropic–nematic transition in the reduced temperature range $1.60 \leq T^* \leq 3.0$ from density-functional theory of freezing and on testing the accuracy of the theory. This allows us to analyze the dependence of the coexistence properties upon changes in temperature. The rest of this article is organized as follows. In section 2, we briefly describe the GB potential model together with the parameterizations employed in the calculations. The procedure for solving the Ornstein–Zernike equation using Percus–Yevick integral equation theory for the calculation of pair-correlation functions of the isotropic phase is described in section 3. Section 4 discusses the essentials of density-functional theory applied to study the freezing of complex fluids into

nematic phase. The article ends with a brief discussion of results given in section 5.

2. GAY–BERNE POTENTIAL

The GB potential model is a sort of anisotropic Lennard–Jones potential that is rapidly becoming a prototype for simulations of liquid crystals. The potential has an attractive and repulsive part decreasing with separation r as r^{-6} and r^{-12} but with a rather complex form that depends on the molecule orientations as well as the intermolecular vector. The anisotropic interaction between two molecules i and j, which we can think as ellipsoids of revolution, with orientations given by unit vectors $\mathbf{e}_i$ and $\mathbf{e}_j$ and with centers separated by the intermolecular vector $\mathbf{r}$, can be written according to the GB model as

$$u(i,j) = U(\mathbf{e}_i, \mathbf{e}_j, \mathbf{r}) = 4\varepsilon(\mathbf{e}_i, \mathbf{e}_j, \hat{\mathbf{r}})\left\{ \left[\frac{\sigma_0}{\mathbf{r} - \sigma(\mathbf{e}_i, \mathbf{e}_j, \hat{r}) + \sigma_0}\right]^{12} - \left[\frac{\sigma_0}{\mathbf{r} - \sigma(\mathbf{e}_i, \mathbf{e}_j, \hat{\mathbf{r}}) + \sigma_0}\right]^{6} \right\} \quad (1)$$

where $\hat{\mathbf{r}}$ is a unit vector along the intermolecular vector. σ_0 is the contact distance when the particles are orthogonal to the intermolecular vector. The parameterization of the potential is rather complex but basically it can be related to shape and attractive energy anisotropy. The information about the shape of the molecules is contained in the orientational dependent range parameter, $\sigma(\mathbf{e}_i, \mathbf{e}_j, \hat{\mathbf{r}})$, that is,

$$\sigma(\mathbf{e}_i, \mathbf{e}_j, \hat{\mathbf{r}}) = \sigma_0\left\{1 - \frac{1}{2}\chi\left[\frac{(\mathbf{e}_i \cdot \hat{\mathbf{r}} + \mathbf{e}_j \cdot \hat{\mathbf{r}})^2}{1 + \chi(\mathbf{e}_i \cdot \mathbf{e}_j)} + \frac{(\mathbf{e}_i \cdot \hat{\mathbf{r}} - \mathbf{e}_j \cdot \hat{\mathbf{r}})^2}{1 - \chi(\mathbf{e}_i \cdot \mathbf{e}_j)}\right]\right\}^{-\frac{1}{2}} \quad (2)$$

where χ is a function of the ratio $x_0(\equiv \sigma_e/\sigma_s)$, which is defined in terms of the contact distances when the molecules are end-to-end (e) and side-by-side (s),

$$\chi = \frac{x_0^2 - 1}{x_0^2 + 1}. \quad (3)$$

This vanishes for a sphere and tends to the limiting value of unity for an infinitely long rod. The orientational dependent strength parameter, $\varepsilon(\mathbf{e}_i, \mathbf{e}_j, \hat{\mathbf{r}})$, is given by a product of two functions,

$$\varepsilon(\mathbf{e}_i, \mathbf{e}_j, \hat{\mathbf{r}}) = \varepsilon_0\ \varepsilon^{\nu}(\mathbf{e}_i, \mathbf{e}_j)\varepsilon'^{\mu}(\mathbf{e}_i, \mathbf{e}_j, \hat{\mathbf{r}}), \quad (4)$$

where the scaling parameter ε_0 is the well depth for the cross configuration. The first of these functions,

$$\varepsilon(\mathbf{e}_i, \mathbf{e}_j) = \left[1 - \chi^2(\mathbf{e}_i \cdot \mathbf{e}_j)^2\right]^{-\frac{1}{2}}, \tag{5}$$

clearly favors the parallel alignment of the particles and so aids liquid-crystalline formation. The second function has a form analogous to $\sigma(\mathbf{e}_i, \mathbf{e}_j, \hat{\mathbf{r}})$, that is,

$$\varepsilon'(\mathbf{e}_i, \mathbf{e}_j, \hat{\mathbf{r}}) = 1 - \frac{1}{2}\chi'\left[\frac{(\mathbf{e}_i \cdot \hat{\mathbf{r}} + \mathbf{e}_j \cdot \hat{\mathbf{r}})^2}{1 + \chi'(\mathbf{e}_i \cdot \mathbf{e}_j)} + \frac{(\mathbf{e}_i \cdot \hat{\mathbf{r}} + \mathbf{e}_j \cdot \hat{\mathbf{r}})^2}{1 - \chi'(\mathbf{e}_i \cdot \mathbf{e}_j)}\right] \tag{6}$$

where the parameter χ' is determined by the ratio of the well depths, $k'(\equiv \varepsilon_s/\varepsilon_e)$, via

$$\chi' = \frac{k'^{1/\mu} - 1}{k'^{1/\mu} + 1}. \tag{7}$$

This second function favors the side-by-side arrangement over the end to end and so encourages the formation of smectic phases. Note that the potential of Eq. (1) reduces to the spherical Lennard–Jones (12-6) potential with parameters σ_0 and ε_0, when both x_0 and k' are equal to unity. In their work, Gay and Berne found a good match with the interaction between a pair of linear arrays of four Lennard–Jones sites by using $x_0 = 3.0$, $k' = 5.0$, $\mu = 2$, and $\nu = 1$.

The GB potential for a certain choice of parameters is conveniently indicated by the notation GB (x_0, k', μ, ν) proposed by Bates and Luckhurst [19]. The potential contains four adjustable parameters that control the anisotropy in the repulsive and attractive interactions in addition to two parameters $(\sigma_0, \varepsilon_0)$ that scale the distance and energy, respectively. Though x_0 measures the anisotropy of the repulsive core, it also determines the difference in the depth of the attractive well between the side-by-side and the cross configurations. Both x_0 and k' play important roles in stabilizing the liquid-crystalline phases. The exact role of other two parameters μ and υ are not very obvious, though they appear to affect the anisotropic attractive forces in a subtle way. Bates and Luckhurst [19] have used the isothermal–isobaric Monte Carlo simulations and have shown that the mesogen GB (4.4,20.0,1,1) exhibits isotropic, nematic, smectic A, and smectic B phases, depending upon the choice of the pressure. Most liquid crystals of technological interest are formed by highly elongated molecules.

3. PAIR-CORRELATION FUNCTIONS OF THE ISOTROPIC PHASE: THE PERCUS–YEVICK THEORY

The pair-correlation functions (PCFs) of the isotropic fluid are of particular interest as they are the lowest order microscopic quantity that contains information about the orientational and translational structures of the system and also have direct contact with intermolecular (as well as with intramolecular) interactions. The values of the PCFs as a function of intermolecular separation and orientations at a given temperature and density are found either by computer simulations or by solving integral equation theories [23–26]. Integral equation methods have been successfully used to study the structural properties of nonspherical isotropic fluids [27–30].

In integral equation theory, we solve the Ornstein–Zernike (OZ) equation

$$h(1,2) - c(1,2) = \gamma(1,2) = \rho_i \int c(1,3)[\gamma(2,3) + c(2,3)]dx_3, \qquad (8)$$

where ρ_i is the number density of the liquids and $i = x_i$ denotes both the location r_i of the center of the ith molecule and its relative orientation Ω_i, described by the Euler angles θ, φ, and ψ with suitable closure relations such as the Percus–Yevick (PY) integral equation, hypernetted-chain (HNC) equation, mean-spherical approximation (MSA), and so forth. Approximations are introduced in the theory through these closure relations. In Eq. (8), $h(1,2) = g(1,2) - 1$ and $c(1,2)$ are, respectively, the total and direct PCFs.

The PY closure relations are written in various equivalent forms; the form we adopt is [29,30]

$$c(1,2) = f(1,2)[1 + \gamma(1,2)] \qquad (9)$$

where

$$f(1,2) = \exp[-\beta u(1,2)] - 1,$$

and $\beta = (k_B T)^{-1}$. Here $u(1,2)$ is a pair potential energy of interaction. Because all the functions appearing in Eqs. (8) and (9) are invariant pairwise functions, they can be expanded in spherical harmonics either in a space-fixed (SF) frame or in a body-fixed (BF) frame. For example, the expansion of direct PCF in a SF frame is written as

$$c(1,2) = c(r_{12}, \Omega_1, \Omega_2) = \sum_{l_1 l_2 l} \sum_{m_1 m_2 m} c_{l_1 l_2 l}(r_{12}) C_g(l_1 l_2 l; m_1 m_2 m) \times Y_{l_1 m_1}(\Omega_1) Y_{l_2 m_2}(\Omega_2) Y^*_{lm}(\hat{r}), \qquad (10)$$

where $C_g(l_1 l_2 l; m_1 m_2 m)$ are the Clebsch–Gordon coefficients.

In the k space, the OZ equation has a particularly simple form in terms of BF spherical harmonic coefficients:

$$\hat{h}_{l_1 l_2 m}(k) = \hat{c}_{l_1 l_2 m}(k) + (-1)^m \frac{\rho_i}{4\pi} \sum_{l_3} \hat{h}_{l_1 l_3 m}(k) \hat{c}_{l_2 l_3 m}(k), \tag{11}$$

where the summation is over allowed values of l_3. Similarly, from Eq. (9) in BF frame we get

$$\begin{aligned} c_{l_1 l_2 m}(r_{12}) = & \sum_{l_1' l_1'' l_2' l_2''} \frac{1}{4\pi} \left[\frac{(2l_1'+1)(2l_1''+1)(2l_2'+1)(2l_2''+1)}{(2l_1+1)(2l_2+1)} \right]^{\frac{1}{2}} \\ & \times C_g(l_1' l_1'' l_1; 000) C_g(l_2' l_2'' l_2; 000) \sum_{m' m''} C_g(l_1' l_1'' l_1; m' m'' m) \\ & \times C_g(l_2' l_2'' l_2; \underline{m}' \underline{m}'' \underline{m}) f_{l_1' l_2' m'}(r_{12}) \left[4\pi \delta_{000}^{l_1'' l_2'' m''} + \gamma_{l_1'' l_2'' m''}(r_{12}) \right] \end{aligned} \tag{12}$$

where $\underline{m} = -m$, and the summation is over allowed values of $l_1', l_1'', l_2', l_2'', m'$, and m''. A similar expression can be written in the SF frame. Numerically one finds it easier to calculate the BF harmonic coefficients than SF harmonic coefficients. The two harmonic coefficients are related through a linear transformation,

$$c_{l_1 l_2 m}(r_{12}) = \sum_l \left[\frac{2l+1}{4\pi} \right]^{\frac{1}{2}} c_{l_1 l_2 l}(r_{12}) C_g(l_1 l_2 l : m \underline{m} 0), \tag{13}$$

or

$$c_{l_1 l_2 l}(r_{12}) = \sum_m \left[\frac{4\pi}{2l+1} \right]^{\frac{1}{2}} c_{l_1 l_2 m}(r_{12}) C_g(l_1 l_2 l; m \underline{m} 0). \tag{14}$$

The iterative numerical solution can be carried out in a manner described elsewhere [29,30]. Note that in any numerical calculation we can handle only a finite number of the spherical harmonic coefficients for each orientation-dependent function. The accuracy of the results depends on this number. As the anisotropy in the shape of the molecules (or in interactions) and the value of liquid density ρ_i increases, more harmonics are needed to get proper convergence. We have included the terms up to l indices equal to 6 though it is desirable to include higher-order harmonics, that is, for $l > 6$, but it will increase the computational time manifold. Our interest is to use the data of the harmonics of pair-correlation functions for freezing transitions where low-order harmonics are generally involved. The only effect the higher-order harmonics appear to have on these low-order harmonics is to modify the finer structure of the harmonics at small values of r

whose contributions to the structural parameters (to be defined later) are negligible.

4. DENSITY-FUNCTIONAL THEORY OF FREEZING FOR NEMATIC PHASE

Density-functional theory (DFT) has been clearly discussed several times in literature [31–34] and the essentials of the approach are well known. In the DFT [34], one uses the grand thermodynamic potential defined as

$$-W = \beta A - \beta\mu_c \int d\mathbf{r}\, d\mathbf{\Omega}\, \rho(\mathbf{r}, \mathbf{\Omega}), \tag{15}$$

where A is the Helmholtz free energy, μ_c is the chemical potential, and $\rho(\mathbf{r}, \mathbf{\Omega})$ is a singlet distribution function, to locate the transition. It is convenient to subtract the isotropic fluid thermodynamic potential from W and write it as [34]

$$\Delta W = W - W_i = \Delta W_1 + \Delta W_2, \tag{16}$$

with

$$\frac{\Delta W_1}{N} = \frac{1}{\rho_i V} \int dr\, d\Omega \left[\rho(r, \Omega) \ln\left(\frac{\rho(r, \Omega)}{\rho_i} \right) - \Delta\rho(r, \Omega) \right] \tag{17}$$

and

$$\frac{\Delta W_2}{N} = -\frac{1}{2\rho_i} \int d\mathbf{r}_{12}\, d\mathbf{\Omega}_1\, d\mathbf{\Omega}_2\, \Delta\rho(\mathbf{r}_1, \mathbf{\Omega}_1)\, c(r_{12}, \mathbf{\Omega}_1, \mathbf{\Omega}_2)\, \Delta\rho(\mathbf{r}_2, \mathbf{\Omega}_2). \tag{18}$$

Here $\Delta\rho(\mathbf{r}, \mathbf{\Omega}) = \rho(\mathbf{r}, \mathbf{\Omega}) - \rho_i$, where ρ_i is the density of the coexisting liquid. The density of the ordered phase can be obtained by minimizing ΔW with respect to arbitrary variation in the ordered phase density subject to the constraint that there is one molecule per lattice site (for perfect crystal) and/or orientational distribution is normalized to unity. Thus,

$$\ln \frac{\rho(\mathbf{r}_1, \mathbf{\Omega}_1)}{\rho_i} = \lambda_L + \int d\mathbf{r}_2\, d\mathbf{\Omega}_2\, c(r_{12}, \Omega_1, \Omega_2; \rho_i)\, \Delta\rho(\mathbf{r}_2, \mathbf{\Omega}_2), \tag{19}$$

where λ_L is a Lagrange multiplier, which appears in the equation because of the constraint imposed on the minimization. To locate the freezing transition, one attempts to find the solution of $\rho(\mathbf{r}, \mathbf{\Omega})$ of Eq. (19), which has symmetry of the ordered phase. Below a certain liquid density, say ρ', the only solution of Eq. (19) is the uniform liquid

solution $\rho(\mathbf{r}, \mathbf{\Omega}) = \rho_i$. Above ρ', a new solution of $\rho(\mathbf{r}, \mathbf{\Omega})$ can be found that corresponds to the ordered phase. The phase with lowest grand potential is taken as the stable phase. The transition point is determined by the condition $\Delta W = 0$. Implicit in this approach is an assumption according to which the system is either entirely liquid or entirely ordered phase; no phase coexistence is permitted. This signifies the mean-field character of the theory.

For axially symmetric molecules, the singlet density of the nematic phase can be written in the form

$$\rho(\mathbf{r}, \mathbf{\Omega}) = \rho_n \, f(\Omega), \tag{20}$$

with

$$\rho_n = \rho_i(1 + \Delta\rho^*) \tag{21}$$

and

$$f(\Omega) = 1 + \sum_{l \geq 2}{}'(2l + 1)\overline{P}_l \, P_l(\cos\theta), \tag{22}$$

where θ describes the orientation of the symmetry axis with respect to the director, $\Delta\rho^* = (\rho_n - \rho_i)/\rho_i$ is the relative change in the density at the transition, and

$$\overline{P}_l = \frac{1}{2}\int_0^\pi f(\Omega) P_l(\cos\theta) \sin\theta \, d\theta \tag{23}$$

is the orientational order parameter of the nematic phase. The prime on the summation in Eq. (22) indicates the condition that l is even. ρ_n is the number density of the nematic phase. The orientational singlet distribution $f(\Omega)$ is normalized to unity; that is,

$$\int d\Omega \, f(\Omega) = 1. \tag{24}$$

For a uniaxial phase of cylindrically symmetric molecules, $f(\Omega)$ depends only on angle θ between the director and the molecular symmetry axis.

It has often been found convenient in the case of the nematic phase to use the following ansatz for $f(\Omega)$:

$$f(\Omega) = A_0 \exp\left[\sum_l \lambda_l \, P_l(\cos\theta)\right]. \tag{25}$$

A_0 is determined from the normalization condition of Eq. (24). In the $\lambda_l \to 0$ limit $f(\Omega) \to 1$ corresponds to the isotropic phase. For finite λ_l, $f(\Omega)$

is peaked about $\theta = 0$ and π; these angles correspond to parallel alignment of the molecules.

The entropy term in Eq. (17) can be reduced to the form

$$\frac{\Delta W_1}{N} = -\Delta\rho^* + \frac{\rho_n}{\rho_i}\left\{\ln\left[\frac{\rho_n A_0}{\rho_i}\right] + \sum_{l\geq 2}{}' \lambda_l \overline{P}_l\right\}. \tag{26}$$

The interaction term $\Delta W_2/N$ is evaluated using Eq. (18) for $f(\Omega)$. Thus

$$\frac{\Delta W_2}{N} = -\frac{\Delta\rho^{*2}}{2}\hat{c}_{00}^0 - \frac{(1+\Delta\rho^*)^2}{2}\sum_{l_1 l_2 \geq 2}{}' \overline{P}_{l_1}\overline{P}_{l_2}\hat{c}_{l_1 l_2}^{(0)},$$

where $\hat{c}_{l_1 l_2}^{(0)}$ is the structural parameter. The structural parameters $\hat{c}_{l_1 l_2}^{(0)}$ for the nematic phase are defined as

$$\hat{c}_{l_1 l_2}^{(0)} = (2l_1+1)(2l_2+1)\rho_i \int d\mathbf{r}_{12} d\boldsymbol{\Omega}_1 d\boldsymbol{\Omega}_2\, c(r_{12},\Omega_1,\Omega_2) P_{l_1}(\cos\theta_1) P_{l_2}(\cos\theta_2). \tag{27}$$

All angles in Eq. (27) refer to the space-fixed z-axis. After simplification, Eq. (27) is written as

$$\hat{c}_{l_1 l_2}^{(0)} = \left[\frac{(2l_1+1)(2l_2+1)}{4\pi}\right]^{\frac{1}{2}} \rho_i C_g(l_1 l_2 0;000) \int dr_{12} r_{12}^2 c_{l_1 l_2 0}(r_{12}). \tag{28}$$

From Eqs. (19) and (10) we find the expression for order parameter as

$$\begin{aligned}(1+\Delta\rho^*)\delta_{l0} + \overline{P}_l = &\int d\Omega_1 P_l(\cos\theta_1) \\ &\times \exp\left[\lambda_L + \rho_i \sum_{l_1 l_2}[(2l_1+1)(2l_2+1)]^{\frac{1}{2}} C_g(l_1 l_2 0;000)\right. \\ &\left. P_l(\cos\theta_1)\overline{P}_l \int dr\ r^2 c_{l_1 l_2 0}(r)\right].\end{aligned} \tag{29}$$

5. RESULTS AND DISCUSSION

The ordered phase (translationally and/ or orientationally) coexists with the isotropic liquid when

$$\left(\frac{\partial}{\partial \xi_i}\right)\left(\frac{\Delta W}{N}\right) = 0, \tag{30}$$

and

$$\frac{\Delta W}{N} = 0. \tag{31}$$

The former is a stability condition, whereas the latter is a phase coexistence condition. The ξ_i are variational parameters appropriate for the phase under investigation. For the nematic phase, the variational parameters are ρ_n, λ_2, and λ_4. The coexisting liquid density, ρ_i, is determined by the condition (31).

5.1. Pair-Correlation Functions

We have solved the PY equation for the GB (4.4,20.0,1,1) fluid at wide range of reduced temperatures $T^*(=k_BT/\varepsilon_0)$ and densities $\eta[=(\pi/6)\rho_f\sigma_0^3x_0]$. In Figs. 1–4 we compare the values of $g(r^*) = 1 + h_{000}(r)/4\pi, g_{220}(r^*), g_{020}(r^*)$, and $g_{221}(r^*)$ in the BF frame, respectively, with those obtained by computer simulations [19] for $\eta = 0.36$ and $T^* = 1.80$. From these figures we find that the PY theory gives values of the harmonic coefficients, which are in good qualitative agreement with the computer simulation results. However, the quantitative agreement is not very satisfactory, particularly for the higher-order harmonic coefficients. The PY peak in $g(r^*)$ is broad and of less height than the one found from the simulation. This indicates that the PY theory is unable to predict the orientational correlations in neighboring molecules. It is seen from this figure that $g(r^*)$ exhibits a maximum

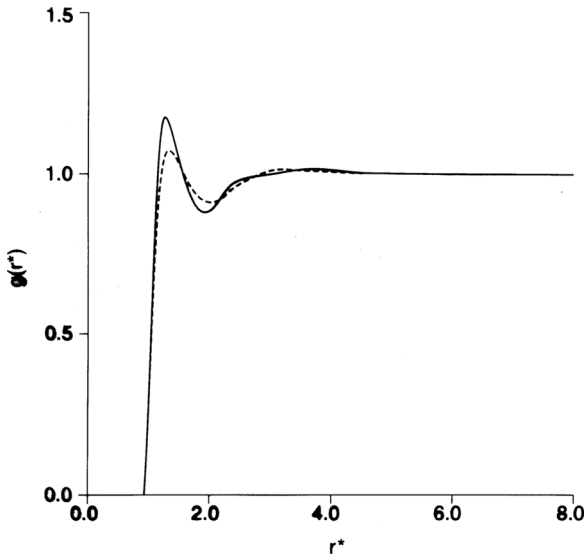

FIGURE 1 Pair-correlation function of the center of mass $g(r^*)$ for GB (4.4,20.0,1,1) fluid at $\eta = 0.36$ and $T^* = 1.80$. The dashed curve is our PY result, and the solid curve is the simulation results of Bates and Luckhurst [19].

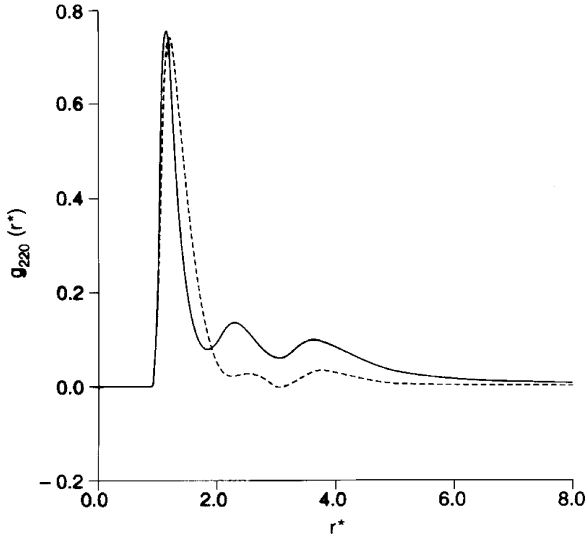

FIGURE 2 Spherical harmonic coefficient $g_{220}(r^*)$ in the body-fixed frame. The curves are the same as in Fig. 1.

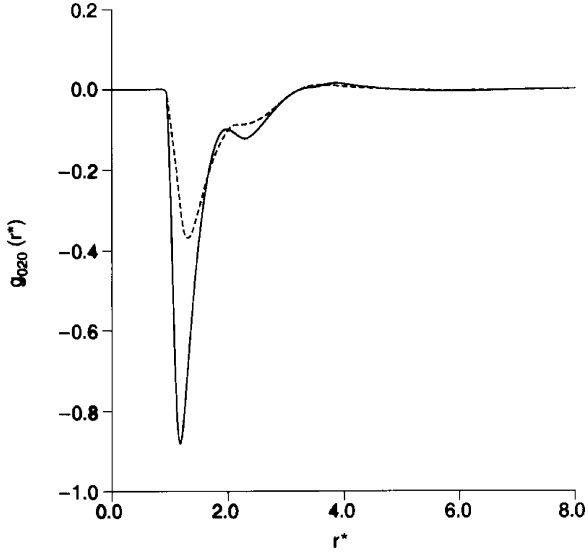

FIGURE 3 Spherical harmonic coefficient $g_{020}(r^*)$ in the body-fixed frame. The curves are the same as in Fig. 1.

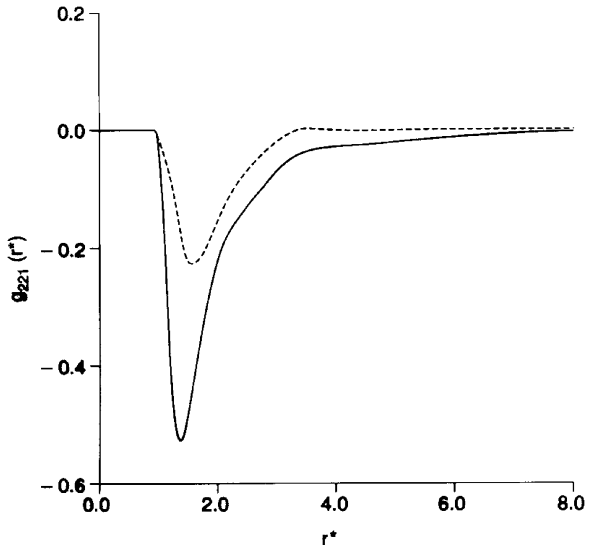

FIGURE 4 Spherical harmonic coefficient $g_{221}(r^*)$ in the body-fixed frame. The curves are the same as in Fig. 1.

at a scaled separation $r^*(=r/\sigma_0)$ just greater than 1.0 corresponding to adjacent molecules lying parallel to each other. Though peak heights in $g_{220}(r^*)$ compare well, the oscillation at large r^* is damped more in PY results than those found in simulation results. This clearly shows that the PY theory underestimates the orientational correlations present in the isotropic phase. From the projections $g_{020}(r^*)$ and $g_{221}(r^*)$ of PCFs, it can be further seen that the PY theory underestimates the orientational correlations. All of the orientational correlation coefficients decay to zero at large r^*, as expected, in the isotropic phase, in accordance with the absence of long-range orientational order. The decay to the long-range limit is complete within a scaled radial separation, r^*, of ~ 6.0, which shows how rapidly the correlations are lost. However, as emphasized in our earlier work, the PY theory is reasonably accurate for the GB potential at low temperatures [22]. In the isotropic phase, the harmonic coefficients have a structure that is analogous to that found from hard ellipsoids with $x_0 = 5.0$ [35]. This similarity is perhaps to be expected, given the ellipsoidal shape of the Gay–Berne molecules.

5.2. Structural and Freezing Parameters

The structural parameters defined by Eq. (27) that appear in the DFT as the input data are obtained from the harmonics of the direct PCFs

TABLE 1 Isotropic–Nematic Freezing Parameters for GB (4.4,20.0,1,1) Fluid (the Reduced Units Are $P^* = P\sigma_0^3/\varepsilon_0, \mu_c^* = \mu_c/\varepsilon_0$, and $\rho^* = \rho\sigma_0^3$

T^*	ρ_i^*	ρ_n^*	$\Delta\rho^*$	$\overline{P}_2$	$\overline{P}_4$	P^*	μ^*	$\hat{c}_{22}^0$	$\hat{c}_{44}^0$
1.60	0.212	0.230	0.088	0.83	0.53	2.57	15.29	4.01	2.07
1.80	0.228	0.244	0.072	0.80	0.50	3.52	20.25	4.05	2.01
2.00	0.242	0.257	0.062	0.78	0.47	4.57	25.50	4.09	1.97
2.20	0.255	0.269	0.055	0.76	0.46	5.72	30.99	4.11	1.92
2.40	0.266	0.279	0.051	0.75	0.44	6.96	36.67	4.13	1.89
2.60	0.276	0.289	0.046	0.74	0.43	8.26	42.51	4.15	1.85
2.80	0.286	0.298	0.043	0.73	0.42	9.64	48.46	4.17	1.83
3.00	0.294	0.306	0.040	0.72	0.41	11.07	54.53	4.18	1.80

evaluated using the PY integral equation theory. Using these values of structural parameters in the DFT, the freezing parameters for GB (4.4,20.0,1,1) fluid have been calculated and listed in Table 1. The model includes (anisotropic) attractive interactions and therefore allows for a systematic study of the effect of varying temperature on liquid-crystalline properties.

In a theory of freezing of molecular liquids into nematic phase, the structural parameters $\hat{c}_{l_1 l_2}^{(0)}$ play important roles. The parameter $\hat{c}_{00}^0$ is related to the isothermal compressibility and $\hat{c}_{22}^0$ and higher-order coefficients to the freezing parameters. The quantities $\hat{c}_{22}^0$ and $\hat{c}_{44}^0$ are found to be very sensitive to the approximations involved in a given integral equation theory. We find that the fluid freezes when the structural parameters $\hat{c}_{22}^0$ and $\hat{c}_{44}^0$ attain values of $\sim$4.0 and $\sim$1.9 respectively (see Table 1). Note that these numbers vary, though very weakly, with T^*; as T^* is increased the value of $\hat{c}_{22}^0$ increases and the value of $\hat{c}_{44}^0$ decreases. The structure of the nematic phase near the transition can therefore be approximated as a calculable perturbation of the structure of the coexisting isotropic liquid. The short-range angular correlation that develops either because of hindered rotation or anisotropy in intermolecular interactions or both is already present in the isotropic phase. When this correlation grows to a certain finite value ($\hat{c}_{22}^0 \sim 4.0$), the isotropic phase becomes unstable and the system spontaneously transforms to a nematic phase, which has long-range orientational ordering. An interesting feature can also be noted from Table 1: the $\hat{c}_{22}^0$ ($\sim$4.0) remains almost constant at the transition as T^* is varied from 1.6 to 3.0.

The thermodynamic stability of the nematic phase with respect to the isotropic phase has been proved for several temperatures above $T^* = 1.60$. In the range of temperatures considered here, the isotropic–nematic transition is found to be weakly first order. The

densities and pressure at coexistence are found to shift to lower values as the temperature is decreased (see Table 1). The computer simulation results [19] do not give any clear indication about how the freezing parameters vary with transition temperature. In Fig. 5, we plot the variation of temperature with isotropic–nematic coexistence densities (ρ^*) and the order parameters, $\overline{P}_n$, respectively, found from the density-functional theory. The theoretical results show that the coexistence densities (ρ_i^*, ρ_n^*) increase with increasing temperature and the fractional density changes, $\Delta\rho^*$, found are rather small, which is consistent with the fact that the molecules are hard and are not very compressible at the transition densities. We observe that the values of the orientational order parameters and the change in density at the transitions are higher than those obtained by computer simulations. The simulation results show that at $T^* = 1.60$, the mesogen GB (4.4,20.0,1,1) forms nematic phase at scaled density $\rho^* = 0.1756$ with orientational order parameters $P_2 = 0.689$ and $P_4 = 0.302$. It has already been pointed out in our earlier work [22] that the second-order DFT has the tendency to overestimate the orientational order parameters and the change in density. The DFT predicts that the

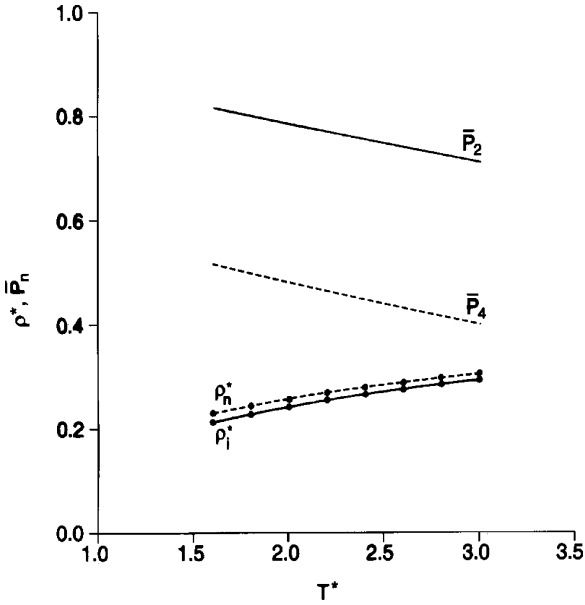

FIGURE 5 Variation of order parameter $\overline{P}_n$ and coexistence densities (ρ_i^*, ρ_n^*) with reduced temperature T^* for GB (4.4,20.0,1,1) fluid. The results are obtained from the DFT using the PY values of correlation functions.

order parameters $\overline{P}_2$ and $\overline{P}_4$ decrease as the transition temperature is increased. The curves reveal quite well the behavior of the nematic order as predicted, for example, by Maier–Saupe theory [36]. The general features of these quantities are in agreement with the experiment.

We have presented here a theoretical study of the GB (4.4,20.0,1,1) fluid focussed on the stability of the isotropic (disordered) and nematic (orientational ordered) liquid crystals at different temperatures. From the results tabulated and graphed, it is obvious that the DFT provides a good description of the properties of the nematic phase. As has already been pointed out in section 5.1, the PY theory gives qualitatively correct results for the PCFs; quantitatively it underestimates the orientational correlations, and this defect of the PY theory becomes more pronounced as temperature is increased. In the conclusion, we emphasize that the freezing transitions in complex fluids can be predicted reasonably well with the density-functional method if the values of the PCFs in the isotropic phase are accurately known.

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