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The Percus–Yevick approximation for quadrupolar molecular fluids

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Abstract

The Percus–Yevick integral equation theory has been solved to study the equilibrium and structural properties of quadrupolar Gay–Berne fluids. The method used involves an expansion of angle-dependent functions appearing in the integral equations in terms of spherical harmonics and the harmonic coefficients are obtained by an iterative algorithm. All the terms of harmonic coefficients which involve l indices up to less than or equal to 6 have been considered. Molecules with length-to-breadth ratios 3.0 and 4.0 have been considered and results are reported for different densities, temperatures, and quadrupole moments. The values of pair correlation functions have been compared with the available computer simulation results.

1. Introduction

The correlation functions which describe the distribution of molecules in a classical fluid can be obtained as the simultaneous solutions of an integral equation, the Ornstein–Zernike (OZ) equation, and a closure relation that relates correlation functions to the pair potential. Well-known closure relations are the Percus–Yevick (PY) relation, the hypernetted chain (HNC) relation, and the mean spherical approximation (MSA) [1, 2]. These methods have made significant contributions to our understanding of simple fluid systems. It is therefore worthwhile to generalize and apply these useful techniques to the study of the liquid crystals that have partial orientational orders. Convenient schemes have been proposed [3, 4] for numerically solving the HNC and PY integral equations for angular-dependent potentials. This accomplishment offers new perspectives for studying, via integral equation theory, the thermodynamic and structural properties of systems of anisotropic molecules, including liquid crystals.

Compared to atomic fluids for which solutions of the OZ equation have been obtained for a variety of pair potentials over wide ranges of temperature and density, the knowledge of correlation functions of a fluid of nonspherical molecules is meagre. The pair correlation functions (PCF) as a function of intermolecular separations and orientations at a given temperature and pressure can be found either by computer

simulation [5–9] or by simultaneous solution of an integral equation, the Ornstein–Zernike equation,

$$h(1, 2) = c(1, 2) + \rho_f \int c(1, 3)h(2, 3) dx_3, \quad (1)$$

where $dx_3 = dr_3 d\Omega_3$, ρ_f is the number density of the fluid, $h(1, 2) = g(1, 2) - 1$ and $c(1, 2)$ are, respectively, the total and direct PCF with suitable closure relations such as the PY, HNC, MSA, etc. Approximations are introduced in the theory through these closure relations. These integral equation theories have been quite successful in describing the structure and thermodynamic properties of isotropic fluids [10–15].

The purpose of this paper is to describe a method which allows the Percus–Yevick integral equation theory to be solved for fluids of nonspherical particles and to give explicit results for pair correlation functions for quadrupolar Gay–Berne (GB) fluids. The paper is presented as follows. Section 2 deals with the form of the pair potential together with the parametrizations employed in calculation. Section 3 deals with the description of the Percus–Yevick integral equation theory to calculate pair and direct correlation functions of the isotropic phase. Discussion of results is presented in section 4.

2. The model potential

The intermolecular potential can be written as the sum of the anisotropic GB potential [16] and the contribution of an

embedded quadrupole along the molecular axis of the prolate ellipsoid,

$$u(1, 2) = U(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) = U^{\text{GB}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) + U^{\text{QQ}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}). \quad (2)$$

The GB potential model is one of the most widely used for the description of phase behaviour of the thermotropic liquid crystals due to its relative simplicity and ability to vary the relative strengths of steric repulsion and anisotropic attraction. It has the shifted Lennard-Jones form with strength and range parameters dependent on the orientations of the molecules and the intermolecular vector. The most common form of the GB potential is written as

$$U^{\text{GB}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) = 4\varepsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) \left\{ \left[\frac{\sigma_0}{r - \sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) + \sigma_0} \right]^{12} - \left[\frac{\sigma_0}{r - \sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) + \sigma_0} \right]^6 \right\}, \quad (3)$$

where $r = |\mathbf{r}_1 - \mathbf{r}_2|$, $\hat{\mathbf{r}} = (\mathbf{r}_1 - \mathbf{r}_2)/r$ is a unit vector along the line joining the centres of masses of molecules 1 and 2, $\hat{\mathbf{u}}_i$ is a unit vector along the axis of symmetry of the i th molecule. The orientation-dependent range parameter $\sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})$ represents the distance (for given molecular orientations) at which the intermolecular potential vanishes, and is given by

$$\sigma(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) = \sigma_0 \left[1 - \frac{\chi}{2} \left\{ \frac{(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}} + \hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}})^2}{1 + \chi \hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2} + \frac{(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}} - \hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}})^2}{1 - \chi \hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2} \right\} \right]^{-1/2}. \quad (4)$$

The parameter defining the molecular anisotropy χ is given by

$$\chi = \frac{x_0^2 - 1}{x_0^2 + 1},$$

where $x_0 (= \sigma_e/\sigma_s)$ is the ratio of the contact distances σ_e and σ_s for the particles in end-to-end (e) and side-by-side (s) arrangements, respectively. Accordingly, the parameter x_0 is a measure of the length-to-breadth ratio of the molecule. It follows then that for a sphere χ vanishes while for an infinitely long rod it is unity and for an infinite disc it is minus one. The scaling parameter σ_0 is a length scale parameter which reflects the molecular size. The orientation-dependent strength parameter $\varepsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})$ represents the strength of the interactions, and its dependence upon the molecular orientation is given by

$$\varepsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) = \varepsilon_0 [\varepsilon_1(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2)]^\nu [\varepsilon_2(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})]^\mu, \quad (5)$$

$$\varepsilon_1(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2) = \left[1 - \chi^2 (\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2)^2 \right]^{-1/2}, \quad (6)$$

$$\varepsilon_2(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) = 1 - \frac{\chi'}{2} \left[\frac{(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}} + \hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}})^2}{1 + \chi' \hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2} + \frac{(\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}} - \hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}})^2}{1 - \chi' \hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2} \right], \quad (7)$$

where the scaling parameter ε_0 is the well depth when the molecules are in the cross configuration ($\hat{\mathbf{u}}_1 \cdot \hat{\mathbf{u}}_2 = \hat{\mathbf{u}}_1 \cdot \hat{\mathbf{r}} = \hat{\mathbf{u}}_2 \cdot \hat{\mathbf{r}} = 0$).

Equation (6) favours the parallel alignment of the particle and so aids liquid crystal formation. The parameter χ' is determined by the ratio of the well depth as

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

The new potential anisotropy parameter k' is defined as $k' = \varepsilon_s/\varepsilon_e$, where ε_s is the minimum of the potential for a pair of parallel molecules placed side-by-side (s) and ε_e is the minimum for molecules placed in an end-to-end (e) configuration. The strength of the interactions depends on the particular choice of the exponents ν and μ entering the definition of $\varepsilon(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}})$ in equation (5). The two parameters ν and μ in the well depth function take different sets of values without affecting the relative well depths for the side-by-side and end-to-end configurations. Originally, these parameters were set to the values $\nu = 1, \mu = 2$ [16]. Note that the potential of equation (3) 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.

The GB model contains four parameters (x_0, k', μ, ν) that determine the anisotropy in the repulsive and attractive forces in addition to two parameters (σ_0, ε_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 configuration. Both x_0 and k' play an important role in stabilizing the liquid crystalline phases. The exact roles of the other two parameters μ and ν are not very obvious; though they appear to affect the anisotropic attractive forces in a subtle way. Varying these parameters gives rise to an infinite number of Gay-Berne potentials. These have been shown to give rise to stable nematic and smectic phases. The computer simulation studies show that this potential has been widely studied for a number of parametrizations [5–7, 17–24] and can be regarded as one of the most important anisotropic potentials in use at present. Some theoretical attempts have also been made to calculate the GB phase diagram using the density-functional approach, perturbation method and virial approximations [25–29].

The second term in equation (2) is the potential due to the electrostatic interactions such as the quadrupole–quadrupole interaction, U^{QQ} [2],

$$U^{\text{QQ}}(\hat{\mathbf{u}}_1, \hat{\mathbf{u}}_2, \hat{\mathbf{r}}) = \frac{3Q^2}{4r^5} \times \left[1 - 5(c_1^2 + c_2^2 + 3c_1^2c_2^2) + 2(s_1s_2c' - 4c_1c_2)^2 \right], \quad (8)$$

where $c_i = \cos \theta_i$, $s_i = \sin \theta_i$, $c' = \cos(\varphi_1 - \varphi_2)$ and Q is the permanent quadrupole moment.

3. Isotropic phase: pair correlation functions

The distribution of molecules in a classical system can be adequately described by one- or two-particle density distributions. The one-particle density distribution $\rho(1)$, defined as

$$\rho(1) = \rho(\mathbf{r}, \Omega) = \left\langle \sum_{i=1} \delta(\mathbf{r} - \mathbf{r}_i) \delta(\Omega - \Omega_i) \right\rangle, \quad (9)$$

where \mathbf{r}_i and Ω_i give the position and the orientation of the i th molecule, the pair of angular bracket represents the ensemble average, and δ is the Dirac function, is constant independent of position and orientation for an isotropic fluid. It therefore contains no information about the structure of the system, but contains most of the structural information of ordered phases such as crystalline solid and liquid crystals. The structural information of an isotropic fluid is contained in the two-particle density distribution $\rho(1, 2)$ that gives the probability of finding simultaneously a molecule in a volume element $d\mathbf{r}_1 d\Omega_1$ centred at (\mathbf{r}_1, Ω_1) and a second molecule in a volume element $d\mathbf{r}_2 d\Omega_2$ centred at (\mathbf{r}_2, Ω_2) . $\rho(1, 2)$ is defined as

$$\rho(1, 2) = \rho(\mathbf{r}_1, \Omega_1, \mathbf{r}_2, \Omega_2) = \left\langle \sum_{i \neq j} \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\Omega_1 - \Omega_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \delta(\Omega_2 - \Omega_j) \right\rangle. \quad (10)$$

The pair correlation function $g(1, 2)$ is related to $\rho(1, 2)$ by the relation

$$g(1, 2) = \frac{\rho(1, 2)}{\rho(1) \rho(2)}. \quad (11)$$

Since in an isotropic fluid $\rho(1) = \rho(2) = \rho_f = \langle N \rangle / V$, where $\langle N \rangle$ is the average number of molecules in volume V ,

$$\rho_f^2 g(\mathbf{r}, \Omega_1, \Omega_2) = \rho(\mathbf{r}, \Omega_1, \Omega_2),$$

where $\mathbf{r} = (\mathbf{r}_2 - \mathbf{r}_1)$. In the isotropic phase, $\rho(1, 2)$ depends only on interparticle distance $|\mathbf{r}_2 - \mathbf{r}_1| = r$, on the orientation of molecules with respect to each other, and on the direction of vector \mathbf{r} ($\hat{\mathbf{r}} = \mathbf{r}/r$ is a unit vector along r). The structure in atomic and molecular fluids is described by the pair correlation function, $g(1, 2)$, which enables one to compute the thermodynamic properties and in addition describe the fluid structure and thus is of fundamental importance to the theory of equilibrium properties of molecular fluids. Because of the large number of variables involved, the complete determination of full $g(1, 2)$ is far from simple and such experimental results are not available to the authors. One usually, therefore, either considers spherical harmonic coefficients of $g(1, 2)$ or a value of $g(1, 2)$ as a function of intermolecular separation r for fixed angular orientations. The various equilibrium properties can be expressed as an integral over $g(1, 2)$ or its spherical harmonic coefficients.

The values of the PCF as a function of intermolecular separation and orientations at a given temperature and pressure are found by solving equation (1). In equation (1), $i = x_i$ indicate both the location r_i of the centre of the i th molecule and its relative orientation Ω_i , described by the Euler angles θ, φ and ψ . $c(1, 2)$ is intrinsically a shorter ranged function than $h(1, 2)$, acting as a kernel in equation (1). Although experiments and simulations do not provide a direct route to this function, it is of equal importance to $h(1, 2)$ in the statistical mechanics of liquids, and there has been a dramatic growth in the interest in $c(1, 2)$ in recent years. This is because of the rapid development of density-functional theories of fluids [30–32]: $c(1, 2)$ is simply related to the excess free

energy F^{ex} of the fluid by functional differentiation with respect to the local density $\rho(1) = \rho(\mathbf{r}_1, \Omega_1)$:

$$c(1, 2) = \frac{\delta^2(-F^{\text{ex}}/k_B T)}{\delta\rho(1) \delta\rho(2)},$$

where k_B is Boltzmann's constant and T the temperature. This expression leads to a variety of theories of both homogeneous and inhomogeneous fluids, mostly based on assumptions regarding $c(1, 2)$ in the system of interest, or in some reference system used as the basis of a perturbation treatment.

The Percus–Yevick closure relation is written in various equivalent forms. The form adopted here is

$$c(1, 2) = f(1, 2) [g(1, 2) - c(1, 2)], \quad (12)$$

where $f(1, 2) = \exp[-\beta u(1, 2)] - 1$ is the Mayer function, $\beta = (k_B T)^{-1}$ and $u(1, 2)$ is a pair potential energy of interaction. Since for the isotropic fluid the direct correlation function (DCF) is an invariant pair-wise function, it has an expansion in body-fixed (BF) frame in terms of basic set of rotational invariants, as

$$c(1, 2) = c(\mathbf{r}_{12}, \Omega_1, \Omega_2) = \sum_{l_1 l_2 m} c_{l_1 l_2 m}(r_{12}) Y_{l_1 m}(\Omega_1) Y_{l_2 \underline{m}}(\Omega_2), \quad (13)$$

where $\underline{m} = -m$. The BF coefficients $c_{l_1 l_2 m}(r_{12})$ are defined as

$$c_{l_1 l_2 m}(r_{12}) = \int c(\mathbf{r}_{12}, \Omega_1, \Omega_2) Y_{l_1 m}^*(\Omega_1) Y_{l_2 \underline{m}}^*(\Omega_2) d\Omega_1 d\Omega_2. \quad (14)$$

Expanding all the angle-dependent functions in BF frame, the OZ equation reduces to a set of algebraic equations in Fourier space.

$$h_{l_1 l_2 m}(k) = c_{l_1 l_2 m}(k) + (-1)^m \frac{\rho_f}{4\pi} \sum_{l_3} c_{l_1 l_3 m}(k) h_{l_3 l_2 m}(k), \quad (15)$$

where the summation is over acceptable values of l_3 . The PY closure relation is expanded in spherical harmonics in the body or space-fixed (SF) frame. The PCF are then found by solving these equations self-consistently [10]. Numerically it is easier to calculate the BF harmonic coefficients than those of SF harmonics. The BF harmonic coefficients $A_{l_1 l_2 m}(r_{12})$ and SF harmonic coefficients $A_{l_1 l_2 l}(r_{12})$ are related through a linear transformation,

$$A_{l_1 l_2 m}(r_{12}) = \sum_l \left[\frac{2l+1}{4\pi} \right]^{\frac{1}{2}} A_{l_1 l_2 l}(r_{12}) C_g(l_1 l_2 l; m \underline{m} 0), \quad (16)$$

or

$$A_{l_1 l_2 l}(r_{12}) = \sum_m \left[\frac{4\pi}{2l+1} \right]^{\frac{1}{2}} A_{l_1 l_2 m}(r_{12}) C_g(l_1 l_2 l; m \underline{m} 0), \quad (17)$$

where $C_g(l_1 l_2 l; m \underline{m} 0)$ are the Clebsch–Gordan coefficients. However, the general function $A(1, 2)$ may be either $h(1, 2)$ or $c(1, 2)$.

In any numerical calculation one can handle only a finite number of spherical harmonic coefficients for each orientation-dependent function. The accuracy of the results depends on

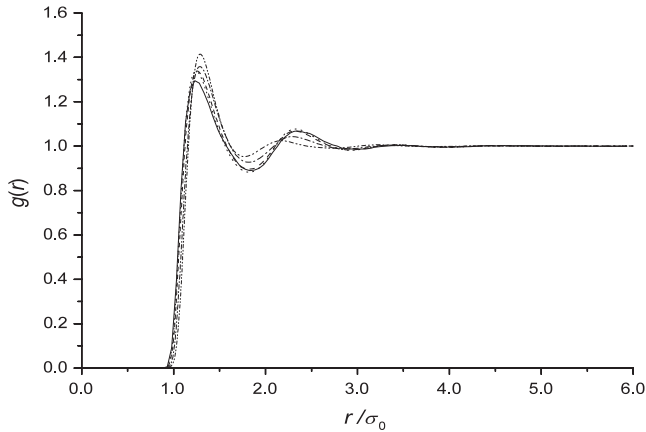


Figure 1. Pair correlation function of the centre of mass $g(r)$ for $x_0 = 3.0$, $k' = 5$, $T^* = 1.25$, and $\eta = 0.45553$. The solid curve is the simulation result of Miguel [6]. The dotted, dashed, dash-dotted, and dash-double dotted curves are PY results for $Q^{*2} = 0.0, 0.5, 1.0$, and 1.5 , respectively.

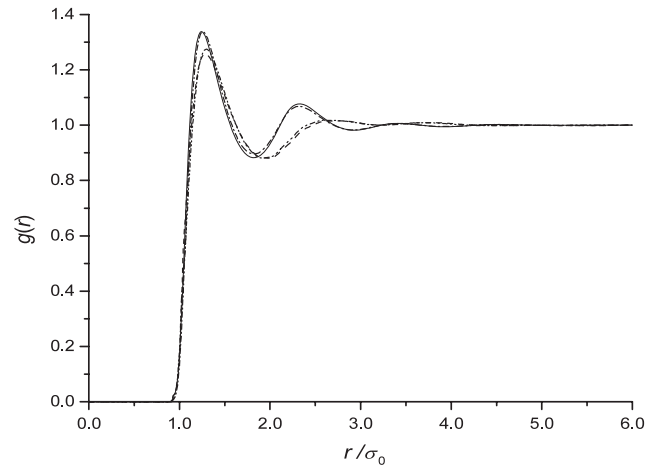


Figure 2. Pair correlation function of the centre of mass $g(r)$ for $\eta = 0.45553$ at $T^* = 1.25$. The solid and dash-dotted curves are PY results for $x_0 = 3.0$ at $Q^{*2} = 0.0$ and 0.5 . The dashed and dash-double dotted curves are PY results for $x_0 = 4.0$ at $Q^{*2} = 0.0$ and 0.5 , respectively.

this number. As the anisotropy in shape of molecules (or in interactions) and the value of fluid density ρ_f increases, more harmonics are needed to get proper convergence. It has been observed that the series converges if it is truncated at the value of l indices equal to 6 for molecules with $x_0 \leq 3.0$ [10], though it is desirable to include higher-order harmonics, i.e. for $l > 6$. However, it will greatly increase the computational time. One can use the data of the harmonics of the DCF for freezing transitions where only 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 (dealt with later) are negligible.

The iterative numerical solution can be carried out in a manner described elsewhere [10]. An appropriate grid width $\Delta r = 0.01$ is chosen in configuration space and the various functions are tabulated on $M = 1024$ grid points, the step size in Fourier space being $\Delta k = \pi/M \Delta r$. All one-dimensional integrals can be conveniently calculated using the trapezoidal rule. The correlation function expansions included all terms for which $l_1, l_2, m \leq 6$ involving a total of 30 independent projections.

4. Results and discussions

4.1. Pair correlation functions

The quadrupolar GB potential model considered here is characterized by anisotropy parameters $x_0 = 3.0$ and 4.0 , $k' = 5$, $\mu = 2$, $\nu = 1$ and the reduced quadrupole moment $Q^* = Q/(4\pi\epsilon_0\sigma_0^5)^{1/2}$. The molecular packing fraction and reduced temperature are given respectively as $\eta = (\pi/6)\rho_f\sigma_0^3$ and $T^* = k_B T/\epsilon_0$. The PY integral equation theory has been solved for quadrupolar GB fluid for a wide range of reduced temperatures and densities at $Q^{*2} = 0.0, 0.5, 1.0$, and 1.5 . In figure 1, the values of $g(r) = 1 + h_{000}(r)/4\pi$ have been compared with computer simulation results of Miguel [6] at

$T^* = 1.25$ and $\eta = 0.45553$. The results obtained from the PY theory are in good qualitative agreement with the simulation results. However, the quantitative agreement needs improvement. The values of $g(r)$ have also been plotted for quadrupole moments $Q^{*2} = 0.0, 0.5, 1.0$, and 1.5 . The effect of the quadrupole on $g(r)$ is to increase the height of the first peak and to delay the distance at which $g(r)$ starts to be different from zero. Clearly, the quadrupolar interactions change the structure of the fluid because of its strong dependence on orientation. Other harmonics of PCF have not been plotted here since no computer simulation results are available to the best of our knowledge.

In figure 2, the values of $g(r)$ for $x_0 = 3.0$ and 4.0 at $T^* = 1.25$ and $\eta = 0.45553$ have been compared for $Q^{*2} = 0.0$ and 0.5 . It is seen from this figure that $g(r)$ exhibits a pronounced maximum at a scaled separation $r^*(=r/\sigma_0)$ just greater than 1.0 corresponding to adjacent particles lying parallel to each other. There is a second, weaker maximum at $r^* \cong 2.3$ and this may be associated with a shell of next nearest neighbours, again with symmetry axes parallel. The structure in the $g(r)$ is lost for longer separations as expected for an isotropic liquid. The structure in $g(r)$ becomes less pronounced as x_0 is increased. This is most likely due to the decreasing tendency of molecules to form parallel configurations. The quadrupole moment slightly modifies the structure of the fluid, as can be seen in the figure.

Figure 3 shows the effect of quadrupole moment and temperature on the structure of the fluid. In figure 3, the values of $g(r)$ have been plotted for $x_0 = 3.0$ at $T^* = 0.95$ and 1.25 , $\eta = 0.45553$ for $Q^{*2} = 0.0$ and 1.5 . The orientational correlation decreases as the temperature increases and the maximum of $g(r)$ is more pronounced with the lowered temperatures. The maximum of $g(r)$ becomes more pronounced and sharper when temperature is lowered and the strength of the quadrupole moment is increased.

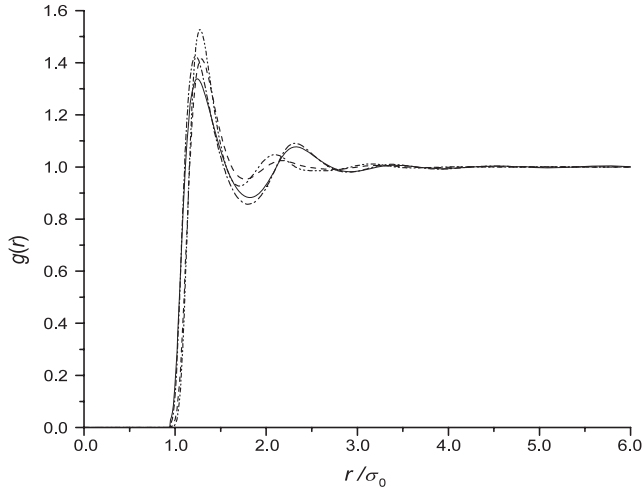


Figure 3. Pair correlation function of the centre of mass $g(r)$ for $x_0 = 3.0$, $k' = 5$, and $\eta = 0.45553$. The solid and dashed curves are PY results for $T^* = 1.25$ at $Q^{*2} = 0.0$ and 1.5 . The dash-dotted and dash-double dotted curves are for $T^* = 0.95$ at $Q^{*2} = 0.0$ and 1.5 , respectively.

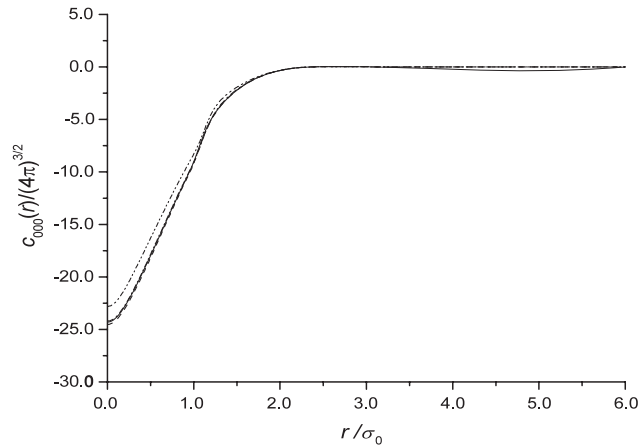


Figure 4. The SF-spherical harmonic coefficient $c_{000}(r)/(4\pi)^{3/2}$ for $x_0 = 3.0$, $k' = 5$, $\eta = 0.45553$, and $T^* = 1.25$. The solid, dashed, dash-dotted, and dash-double dotted curves are PY results for $Q^{*2} = 0.0, 0.5, 1.0$, and 1.5 , respectively.

4.2. Direct correlation functions

The direct correlation functions are a central quantity in theories of liquid matter and play an important role in the density-functional theory (DFT). In the DFT, the free energy and the grand potential of a classical system as a functional expansion of one-particle density is convenient to study the structural and thermodynamical properties of homogeneous and inhomogeneous fluids [31–33]. In the theory of molecular fluids, the direct correlation functions can be used to calculate the equation of state, free energy, phase transition, elastic constants, etc.

In figures 4–6, the SF c -harmonics $c_{000}(r)$, $c_{220}(r)$, and $c_{440}(r)$ obtained by the PY approximation and scaled by $(4\pi)^{3/2}$ have been plotted, respectively, for each value of $Q^{*2} = 0.0, 0.5, 1.0$, and 1.5 for $x_0 = 3.0$, $\eta = 0.45553$ and $T^* = 1.25$. It is to be noted that these

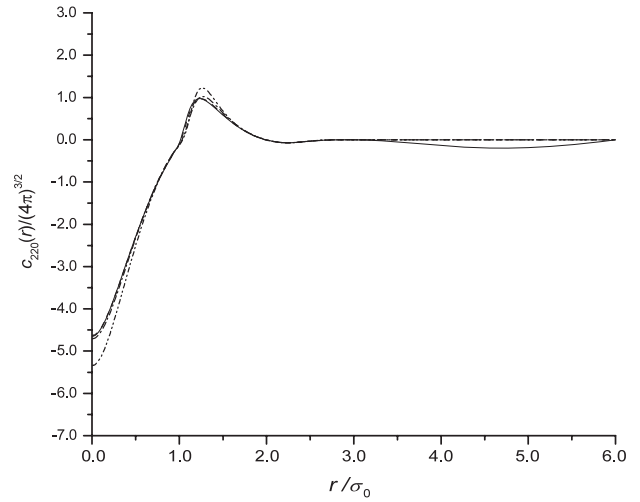


Figure 5. The same as in figure 4, but for $c_{220}(r)/(4\pi)^{3/2}$.

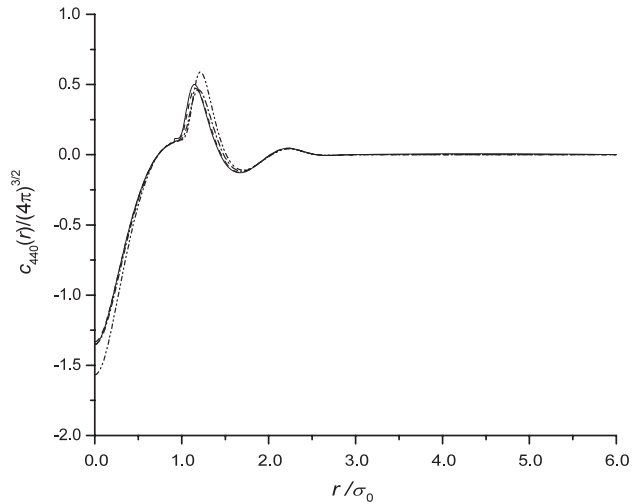


Figure 6. The same as in figure 4, but for $c_{440}(r)/(4\pi)^{3/2}$.

functions are short ranged and decaying very quickly outside the region $r/\sigma_0 \geq 3.0$. The amplitudes of $c_{220}(r)$ and $c_{440}(r)$ within the molecular core increase slightly as the value of quadrupole moment is increased. A similar feature has been reported for the quadrupolar hard Gaussian overlap (HGO) model by Sushma *et al* [34]. The direct correlation functions $c_{000}(r)$, $c_{220}(r)$, and $c_{440}(r)$ can be related to structural parameters (to be defined below) which enter in the density-functional theory as an input parameter to locate the isotropic–nematic transition and calculate freezing parameters. When the strength of quadrupole moment increases, the isotropic–nematic transition densities shifted towards lower fluid densities. This is because $c_{000}(r)$ harmonics takes less negative values while $c_{220}(r)$ and $c_{440}(r)$ take more negative values. This increase in negative values of c -harmonics decreases the positive contribution of structural parameters which lowers the isotropic–nematic transition densities. The curves plotted in figures 4–6 reveal the same nature shown by Allen *et al* [35].

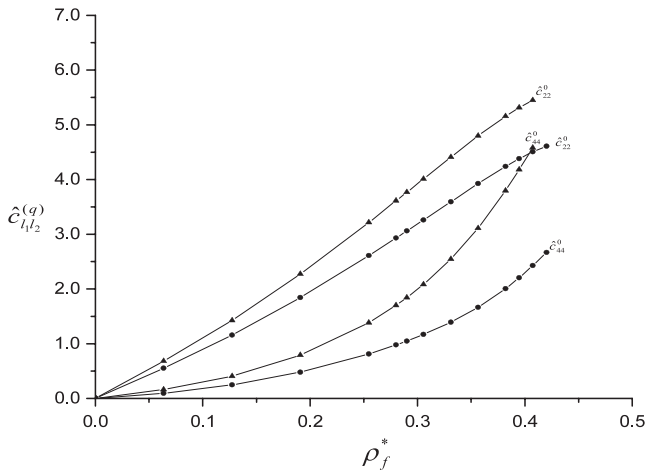


Figure 7. The structural parameter $\hat{c}_{l_1 l_2}^{(0)}$ for $x_0 = 3.0$ at $T^* = 1.25$. The curves with circles and triangles are for $Q^{*2} = 0.0$ and 1.5 , respectively.

In a theory of freezing of molecular fluids into nematic phase the structural parameter $\hat{c}_{l_1 l_2}^{(0)}$ defined as [32],

$$\hat{c}_{l_1 l_2}^{(0)} = (2l_1 + 1) (2l_2 + 2) \rho_f \int d\mathbf{r}_{12} d\Omega_1 d\Omega_2 c(\mathbf{r}_{12}, \Omega_1, \Omega_2) \times P_{l_1}(\cos \theta_1) P_{l_2}(\cos \theta_2), \quad (18)$$

plays an important role. Here P_l is a Legendre polynomial of degree l and angles refer to a space-fixed z -axis, wherein $\hat{c}_{00}^{(0)}$ is related to the isothermal compressibility and $\hat{c}_{22}^{(0)}$ and the higher-order coefficients are related to the freezing parameters. The quantities $\hat{c}_{22}^{(0)}$ and $\hat{c}_{44}^{(0)}$ are found to be very sensitive to the approximation involved in a given integral equation theory. Figure 7 shows the values of structural parameters $\hat{c}_{22}^{(0)}$ and $\hat{c}_{44}^{(0)}$ found from the PY approximation plotted against $\rho_f^* (= \rho_f \sigma_0^3)$ for $x_0 = 3.0$, $T^* = 1.25$, and at $Q^{*2} = 0.0$ and 1.5 . It is seen from this figure that the values of $\hat{c}_{LL}^{(0)}$ increase with density and deviate from low density linear behaviour and increase steeply in the vicinity of the phase transition. These steep increases can in fact be related to the growth of long-range correlations. Clearly, as Q^{*2} increases the phase stability decreases towards lower fluid densities and the isotropic–nematic transitions take place at lower densities. Note that the $\hat{c}_{LL}^{(0)}$ curves for fluids of hard ellipsoids of revolution (HER) and spherocylinders [36, 10] for $x_0 \geq 3.0$ (or $x_0 = 1/3$ in the oblate case) are very similar to those shown in figure 7, and that remarks made above apply equally to those systems. Both HNC and PY approximations have been solved for HER [10, 13] and the PY theory is believed to underestimate the angle-dependent part of the PCF while the HNC theory overestimates them. For PY theory it is found that the isotropic phase remains stable even at very high densities. It is possible that the PY theory would eventually give a transition if numerical solutions could be obtained at higher values of ρ_f^* . It is likely, however, that such a transition would lie above freezing density.

A meaningful attempt has been made herein, so far as theoretical descriptions of understanding the equilibrium properties of a fluid of quadrupolar Gay–Berne fluid are

concerned. In the case of fluids of axially symmetric nonspherical molecules, the angle-dependent pair correlation function can be expanded in products of spherical harmonics. All terms of harmonic coefficients which involve l indices up to less than or equal to 6 have been considered. It can be noticed that solution of the PY integral equation is of considerable interest in the study of the structure and thermodynamic properties of fluids as they are usually accurate and require much less computational effort than approaches based on Monte Carlo (MC), and molecular dynamics (MD) methods. Integral equations can be applied economically to a much broader range of problems than MC and MD methods.

The effect of quadrupole moments on the equilibrium and structural properties of quadrupolar Gay–Berne fluid has been discussed. It is found that the peaks at short range of PCF of the centre of mass become sharper as the value of quadrupole moment is increased. Quadrupolar molecular fluids are much more difficult to treat theoretically and understanding the behaviour of anisotropic fluid systems is a continuing theoretical challenge.

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