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Solution of the Percus-Yevick equation for pair-correlation functions of molecular fluids

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The Percus-Yevick (PY) integral equation has been solved for two model fluids: (i) a fluid of hard ellipsoids of a revolution represented by a Gaussian overlap model, and (ii) a fluid the molecules of which interact via a Gay-Berne [J. Chem. Phys. **74**, 3316 (1981)] model potential. The method used involves an expansion of angle dependent functions appearing in the integral equation in terms of spherical harmonics. The dependence of the accuracy of the results on the number of terms taken in the basis set is explored for both fluids at different densities, temperatures, and lengths to width ratios of the molecules. We have compared our results with those of computer simulations wherever they are available. We find that the PY theory gives reasonable values of the harmonic coefficients for both fluids at all fluid densities when all terms involving the index l up to six in the expansion are considered. For the Gay-Berne fluid we have developed a perturbation expansion for a calculation of the structure and thermodynamic properties of the isotropic phase.

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I. INTRODUCTION

Molecular fluids have both translational and orientational structures and, in general, these two structures are correlated. Pair correlation functions (PCF's) are the lowest order microscopic quantities which contain this information and have direct contact with underlying inter- and intra-molecular interactions [1,2]. The PCF's are found either by computer simulations or by semianalytic approximate methods [3]. In the latter approach one solves the Ornstein-Zernike (OZ) equation,

$$h(1,2)=c(1,2)+\rho_f\int c(1,3)h(2,3)dx_3\ , \tag{1.1}$$

where $i=x_i$ indicates 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), mean spherical approximation (MSA), etc. Approximations are introduced through these closure relations. In Eq. (1.1), $h(1,2)=g(1,2)-1$ and $c(1,2)$ are, respectively, the total and direct PCF's.

Once the PCF's as a function of inter-molecular separation and orientations are known, the equilibrium properties are computed easily [3]. If we assume pairwise additivity of the potential energy of the interactions, all thermodynamic quantities of the system are expressed in terms of the PCF's. In case of nonuniformity [4] or departure from the assumption of pairwise additivity [5] of the potential, one needs to know higher order correlation functions.

Two rather different approaches for finding PCF's of molecular fluids have emerged in recent years. In one of the methods, the PCF's are expanded in a series of angle dependent basic functions (spherical harmonics in the case of linear molecules and generalized harmonics or Wigner rotation matrices in the case of nonlinear molecules). When such expansions of PCF's are substituted in the OZ equation, it reduces to a set of algebraically coupled equations relating the harmonic coefficients of the direct and total correlation functions. These equations involve only one variable (r or k) in place of five or more variables in the original OZ equation.

In another approach one first constructs models in which a molecule is represented by a set of discrete interaction sites that are commonly, but not invariably, located at the sites of the atomic nuclei [6]. The total potential energy of two molecules is obtained as the sum of the spherically symmetric interaction sites potential, the latter one typically of the same form as the potential used for atomic systems. When an interaction-site model is used to represent the intermolecular potential, the natural way to describe the structure of the fluid is in terms of site-site distribution functions $g_{\alpha\beta}(r)$. In any real molecular fluid the most important site-site distribution functions are those that describe the distribution of atomic sites. The correlation function $g_{\alpha\beta}(r)$ is given by the integral of correlation function $g(1,2)=1+h(1,2)$ over all coordinates subject to the constraint that the separation of site α in one molecule and site β in another molecule is equal to r.

Since in this paper we are concerned with systems consisting of rigid molecules of well defined geometry, we use the first method, i.e., the method which uses the angle dependent basis set to expand PCF's and solve the resulting OZ equation. For this we use the PY closure relation and solve the OZ equation for (i) a system of hard ellipsoids of revolution (HER) and for (ii) a system, the molecules of which interact via a Gay and Berne (hereafter referred to as GB) pair potential [7].

The motivation for studying these systems stems from the fact that they capture some of the basic features of the real ordered phases. For example, a system of HER is found [8] to exhibit four distinct phases, viz., isotropic fluid, nematic fluid, plastic solid, and ordered solid. The computer simulation results [9,10] show that the GB potential is capable of forming nematic, smectic A, smectic B, and an ordered solid in addition to the isotropic liquid.

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In the density functional theory of freezing the ordered phase properties are expressed in terms of the direct PCF (DPCF) of an isotropic fluid [4]. The knowledge of the PCF of the isotropic phase as a function of the temperature and density is therefore prerequisite to understanding the transition and stability of the various ordered phases and to calculating the freezing parameters.

The GB potential model is written as

$$u(1,2)=4\epsilon(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)\left[\left[\frac{\sigma_0}{r_{12}-\sigma(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)+\sigma_0}\right]^{12}-\left[\frac{\sigma_0}{r_{12}-\sigma(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)+\sigma_0}\right]^{6}\right], \tag{1.2}$$

where $\hat{\mathbf{r}}_{12}$ is a unit vector along $r_{12}=r_2-r_1$. Here $\epsilon(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)$ and $\sigma(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)$ are angle dependent strength and range parameters, respectively, and are defined as

$$\epsilon(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)=\epsilon_0[1-\chi^2(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)^2]^{-1/2}\left\{1-\chi'\frac{(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_1)^2+(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_2)^2-2\chi'(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_1)(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_2)}{1-\chi'^2(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)^2}\right\}^2, \tag{1.3}$$

$$\sigma(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)=\sigma_0\xi(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)\ , \tag{1.4a}$$

with

$$\xi(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)=\left[1-\chi\frac{(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_1)^2+(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_2)^2-2\chi(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_1)(\hat{\mathbf{r}}_{12}\cdot\hat{\mathbf{e}}_2)}{1-\chi^2(\hat{\mathbf{e}}_1\cdot\hat{\mathbf{e}}_2)^2}\right]^{-1/2}, \tag{1.4b}$$

where $\hat{\mathbf{e}}_1$ and $\hat{\mathbf{e}}_2$ are the unit vectors along the symmetry axes of two interacting molecules. ϵ_0 and σ_0 are constants and, in some ways, provide a measure of the attractive interactions and the size of the molecules. The anisotropy parameters χ and χ' are defined as

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

and

$$\chi'=\frac{k'^{1/2}-1}{k'^{1/2}+1}\ , \tag{1.5}$$

where $x_0(=2a/2b)$ is the length (major axis) to breadth (minor axis) ratio of these molecules and k' is the ratio of the potential well depths for the side-by-side and end-to-end configurations. Note that the potential of Eq. (1.2) 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 potential model was originally proposed as a numerical fit to a four site-site Lennard-Jones (12-6) model and gives a reasonable account of both the anisotropic repulsive and attractive forces. The relative simplicity of the GB model compared with the site-site models makes this model attractive from a computational point of view. Recently, Miguel and co-workers [9] have generated data for PCF's using molecular dynamics (MD) computer simulations. These workers have also shown the subtle role played by the soft repulsion and attraction parts in stabilizing the orientationally ordered phases at low temperatures and high densities.

In a previous paper [11] we solved the OZ equation using the PY closure relation for a system of hard ellipsoids of revolution (HER) considering all harmonic coefficients up to l indices (see Sec. II and Table I for a definition) 4. In this paper we extend this calculation and include all harmonics up to l indices 6. This amounts to considering 30 harmonic coefficients each for an h and c function as compared to 14 in our previous work [11]. It may be noted that in any numerical solution of Eq. (1.1) the accuracy of the results depends on the number of spherical harmonic coefficients for each orientation-dependent function. As the anisotropy in the shape of the molecule (or in the interaction) and the value of fluid density ρ_f increase, higher-order harmonic coefficients are needed to get proper convergence. The comparison of the results of these two calculations therefore enables us to comment on the convergence of the expansion series as the anisotropy in the shape of molecule and fluid density is increased.

The potential energy of the interaction of a pair of HER is represented as

$$u(1,2)=\begin{cases}\infty & \text{for } r_{12}<D(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)\\ 0 & \text{for } r_{12}\geq D(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)\ ,\end{cases} \tag{1.6}$$

where $D(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)$ is the distance of closest approach of two molecules with orientations Ω_1 and Ω_2 in a direction given by $\hat{\mathbf{r}}_{12}$. For $D(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)$ we use the expression given by the Gaussian overlap model of Berne and Pechukas [12], i.e.,

TABLE I. The terms included in different basis sets in BF expansion.

Basis set	No. of independent terms	Terms included[a]
I ($m\leq 4$)	14	000, 200, 220, 221, 222, 400, 420, 421, 422, 440, 441, 442, 443, 444
I ($m\leq 6$)	30	600, 620, 621, 622, 640, 641, 642, 643, 644, 660, 661, 662, 663, 664, 665, 666

[a] Only additional terms which occur in each basis set.

$$D(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)=d_0\xi(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)\ , \tag{1.7}$$

where $d_0=2b$, the minor axis of the ellipsoid, and the angle dependent function $\xi(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)$ is given by Eq. (1.4b).

The paper is organized as follows. In Sec. II, we describe the procedure for solving the OZ equation using the PY closure relation and a method in which the PCF's are expanded in a series of spherical harmonics. Section III is devoted to developing a thermodynamic perturbation method for the calculation of structure and thermodynamic properties of the GB fluid. Here we generalize the approach of Weeks, Chandler, and Anderson [13] for atomic fluid to molecular fluid to molecular fluid and derive an expression for the DPCF of the isotropic fluid consistent with the first order perturbation theory. In Sec. IV we discuss the results for both fluids and comment on the convergence of the expansion series of the PCF's in terms of spherical harmonics. We also compare our results with those of the computer simulations wherever the latter are available. The paper ends with a brief summary and the conclusions of our results given in Sec. V.

II. PAIR CORRELATION FUNCTIONS: PY THEORY

The PY closure relations are written in various equivalent forms; the form which we adopt is [11]

$$c(1,2)=b(1,2)g(1,2)=f(1,2)[g(1,2)-c(1,2)]\ , \tag{2.1}$$

where

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

and

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

Here $u(1,2)$ is a pair potential energy of interaction. Since all the functions appearing in Eqs. (1.1) and (2.1) are an invariant pairwise function, 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 DPCF in an SF frame is written as

$$c(r_{12},\Omega_1,\Omega_2)=\sum_{l_1l_2l}\ \sum_{m_1m_2m} c_{l_1l_2l}(r_{12})C_g(l_1l_2l;m_1m_2m) \times Y_{l_1m_1}(\Omega_1)Y_{l_2m_2}(\Omega_2)Y^*_{lm}(\hat{\mathbf{r}})\ , \tag{2.2}$$

where $C_g(l_1l_2l;m_1m_2m)$ are the Clebsch-Gordan coefficients.

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

$$\hat{h}_{l_1l_2m}(k)-\hat{c}_{l_1l_2m}(k)=\hat{\gamma}_{l_1l_2m}(k)=(-1)^m\frac{\rho_f}{4\pi}\sum_{l_3}\hat{c}_{l_1l_3m}(k)[\hat{c}_{l_3l_2m}(k)+\hat{\gamma}_{l_3l_2m}(k)]\ , \tag{2.3}$$

where the summation is over allowed values of l_3. Similarly, from Eq. (2.1) we get in the BF frame

$$c_{l_1l_2m}(r_{12})=\sum_{l'_1,l''_1,l'_2,l''_2}\frac{1}{4\pi}\left[\frac{(2l'_1+1)(2l'_2+1)(2l''_1+1)(2l''_2+1)}{(2l_1+1)(2l_2+1)}\right]^{1/2}C_g(l'_1l''_1l_1;000)C_g(l'_2l''_2l_2;000)$$
$$\times\sum_{m',m''}C_g(l'_1l''_1l_1;m'm''m)C_g(l'_2l''_2l_2;\underline{m}'\underline{m}''\underline{m})f_{l'_1l'_2m'}(r_{12})[4\pi\delta_{000}^{l''_1l''_2m''}+\gamma_{l''_1l''_2m''}(r_{12})]\ , \tag{2.4}$$

where $\underline{m}=-m$, $\gamma(1,2)=h(1,2)-c(1,2)$, 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. However, one finds it easier to numerically calculate BF harmonic coefficients than SF harmonic coefficients. The two harmonic coefficients are related through a linear transformation,

$$A_{l_1l_2m}(r_{12})=\sum_{l}\left[\frac{2l+1}{4\pi}\right]^{1/2}A_{l_1l_2l}(r_{12})C_g(l_1l_2l;m\underline{m}0)\ ,$$

or

$$A_{l_1l_2l}(r_{12})=\sum_{m}\left[\frac{4\pi}{2l+1}\right]^{1/2}A_{l_1l_2m}(r_{12})C_g(l_1l_2l;m\underline{m}0)\ . \tag{2.5}$$

The general function $A(1,2)$ may be either $h(1,2)$ or $c(1,2)$.

The iterative numerical solution can be carried out in a manner described elsewhere [11]. 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 iterative cycle is started by making initial guesses for the coefficients $c_{l_1l_2m}(r_{12})$. The iteration proceeds as follows:

$$c_{l_1l_2m}(r_{12})^{(i)}\xrightarrow[\text{OZ}]{}\gamma_{l_1l_2m}(r_{12})\xrightarrow[\text{PY}]{}c_{l_1l_2m}(r_{12})^{(\text{new})}\ ,$$

where the superscript (i) denotes the ith iteration. After both steps $c_{l_1l_2m}(r_{12})^{(i)}$ and $c_{l_1l_2m}(r_{12})^{(\text{new})}$ are compared, and if they agree with the desired accuracy (here we take the maximum difference to be less than 10^{-3}), the iteration is terminated. If they do not satisfy this criterion then the $(i+1)$th approximation is obtained by mixing the "ith" and the "new" values according to the equation

$$c_{l_1 l_2 m}(r_{12})^{(i+1)}=\alpha c_{l_1 l_2 m}(r_{12})^{(i)}+(1-\alpha)c_{l_1 l_2 m}(r_{12})^{(\mathrm{new})} ,$$

where α is the mixing parameter adjusted in the range $0<\alpha<1$. The function of the mixing parameter is to avoid large differences between successive iterates and hence prevent divergence.

In Table I we list the two sets of number of terms included in rotational invariant expansion of the correlation functions used in the calculation. In Sec. IV we compare these results for both potential models and draw conclusions on the convergence of the expansion.

III. THERMODYNAMIC PERTURBATION EXPANSION FOR THE GB SYSTEM

The perturbation method of Weeks, Chandler, and Anderson (WCA) [13] of atomic fluids can be generalized to calculate the structure and thermodynamics properties of a GB fluid. For this, we divide the pair potential of Eq. (1.2) into reference and perturbation parts as below:

$$u_r(r_{12},\Omega_1,\Omega_2)=\begin{cases} u(r_{12},\Omega_1,\Omega_2)+\epsilon(\hat{\mathbf{r}}_{12},\Omega_{12}) & \text{for } r_{12}\le r_m(\Omega_{12}) \\ 0 \quad \text{for } r_{12}>r_m(\Omega_{12}) , \end{cases} \tag{3.1}$$

$$u_p(r_{12},\Omega_1,\Omega_2)=\begin{cases} -\epsilon(\hat{\mathbf{r}}_{12},\Omega_{12}) & \text{for } r_{12}\le r_m(\Omega_{12}) \\ u(r_{12},\Omega_1,\Omega_2) & \text{for } r_{12}>r_m(\Omega_{12}) , \end{cases} \tag{3.2}$$

where $r_m(\Omega_{12})=2^{1/6}\sigma_0+\sigma(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)-\sigma_0$ is the separation distance at the minimum.

In terms of these potentials the excess Helmholtz free energy correct to first-order perturbation for a nonuniform system is found to be [14]

$$\Delta A[\rho,u]=\Delta A[\rho,u_{\mathrm{HC}}] -\tfrac{1}{2}\int dx_1\rho(1)\int dx_2\rho(2)[y_{\mathrm{HC}}(1,2)\Delta\phi_{r,\mathrm{HC}} -\beta g_r(1,2)] , \tag{3.3}$$

where $\Delta A[\rho,u_{\mathrm{HC}}]$ is the reduced excess free energy of an *effective* fluid of hard core interacting via a pair potential u_{HC}, which has a form given by Eq. (1.6), and $g_r(1,2)$ is the PCF of the reference system. Other notations appearing in the above equation are as follows:

$$y_{\mathrm{HC}}(1,2)e^{-\beta u_{\mathrm{HC}}(1,2)}=g_{\mathrm{HC}}(1,2) , \tag{3.4}$$

$$\Delta\phi_{r,\mathrm{HC}}=\phi_r-\phi_{\mathrm{HC}},\quad \phi_r=\exp[-\beta u_r(1,2)] ,$$

and

$$\phi_{\mathrm{HC}}=\exp[-\beta u_{\mathrm{HC}}(1,2)] .$$

At this level of approximation the pair correlation function of the fluid is written as

$$g(1,2)\simeq g_r(1,2)=e^{-\beta u_r(1,2)}y_{\mathrm{HC}}(1,2) , \tag{3.5}$$

which may be considered as the zeroth-order approximation for the PCF. The first-order correction arising due to the $u_p(1,2)$ part of the potential involves the higher-order correlation function of the reference system [3,15] and, therefore, is not attempted here.

Since the OZ DPCF is related to the second functional derivative of ΔA, i.e.,

$$c(1,2)=-\frac{\delta^2\Delta A}{\delta\rho(x_1)\delta\rho(x_2)} ,$$

we find from Eq. (3.3)

$$c(1,2)=c_{\mathrm{HC}}(1,2)+\Delta\phi_{r,\mathrm{HC}}y_{\mathrm{HC}}(1,2)-\beta u_p(1,2)g_r(1,2) . \tag{3.6}$$

The first term of the above equation is the DPCF of the fluid of hard core at packing fraction

$$\eta_{\mathrm{HC}}=\tfrac{1}{6}\pi\rho^* x_0(d_0^*)^3 , \tag{3.7}$$

where $\rho^*=\rho_f\sigma_0^3$ and $v_{\mathrm{HC}}=(\pi/6)x_0 d_0^3$ is the volume element of *effective* hard ellipsoids. The distance of closest approach of two HER is reduced in terms of $\sigma(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)$, i.e.,

$$D(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)/\sigma(\hat{\mathbf{r}}_{12},\Omega_1,\Omega_2)=\frac{d_0}{\sigma_0}=d_0^* . \tag{3.8}$$

The value of d_0^* is determined from the condition

$$\int dr_{12}\int d\Omega_1\int d\Omega_2 y_{HC}(r_{12},\Omega_2,\Omega_2)\Delta\phi(r_{12},\Omega_1,\Omega_2)=0 . \tag{3.9}$$

Expanding the angle-dependent functions of Eq. (3.9) in a BF frame and evaluating the integrals using the orthonormal properties of the spherical harmonics, we get

$$\sum_{l_1 l_2 m}(2l_1+1)(2l_2+1)C_g(l_1l_10;000)C_g(l_2l_20;000)C_g(l_1l_10;m\underline{m}0) \times C_g(l_2l_20;\underline{m}m0)\int_0^\infty y_{\mathrm{HC},l_1l_2m}(r_{12})[e_{r,l_1l_2m}(r_{12})-e_{\mathrm{HC},l_1l_2m}(r_{12})]r_{12}^2dr_{12}=0 , \tag{3.10}$$

where $e_{l_1 l_2 m}(r_{12})$ denotes $[\exp(-\beta u)]_{l_1 l_2 m}$. Using the values of $y_{\mathrm{HC},l_1 l_2 m}(r_{12})$ found from the PY theory for HER, we solved Eq. (3.10) to determine the value of d_0^*. The result is given in Sec. IV.

The second and third terms in Eq. (3.6) arise due to softness in the repulsive core and the attractive part of the interaction, respectively. Since the structure of dense fluids is primarily controlled by that part of the interaction that gives rise to a repulsive force, the first-order perturbation theory is expected to yield satisfactory results for dense fluids [2,3].

IV. RESULTS AND DISCUSSION

A. HER model

In Figs. 1–3 we compare the values of $g(r)=1+h_{0000}(r)/4\pi$ of the BF frame of the two basis sets for $x_0=2$ and 3. In these figures we also plot molecular dynamics (MD) simulation results of Talbot, Perera, and Patey [16]. Their model for ellipsoids overlap, however, differs from the Gaussian model of Eq. (1.6) used by us. It is therefore reasonable to expect that the difference in the values of these two results may partly be due to the difference in the overlap model. The computer simulation results for harmonics of PCF's for the Gaussian model of HER overlap are, to the best of our knowledge, not available at present.

Perera, Kusalik, and Patey [17] have solved the PY and HNC equation for HER using the model for ellipsoid overlap used in the MD simulation of Talbot, Perera, and Patey [16]. Both the PY and HNC theories were found to give results for PCF which are in reasonable agreement with the MD results for prolate molecules. In the figures plotted here we do not show the results of Perera, Kusalik, and Patey [17] for the reason stated above.

It may be seen from these figures that for both $x_0=2$ and 3 the basis sets I and II give almost identical results for $g(r)=1+h_{000}(r)/4\pi$ for all values of r/d_0 at low densities (i.e., at $\eta\leq 0.3702$). However, for harmonics involving an l index of 4 or higher our results show that the two basis sets give results which differ from each other. The difference becomes more pronounced at larger x_0, indicating that at large x_0 more terms in the basis set are needed for the proper convergence of the series of PCF's compared to smaller x_0 at the same density. Another feature that appears from our result is that the two basis sets at high densities (i.e., at $\eta=0.592\,38$) give almost identical values for harmonics of PCF's around the first peak but differ at larger separation.

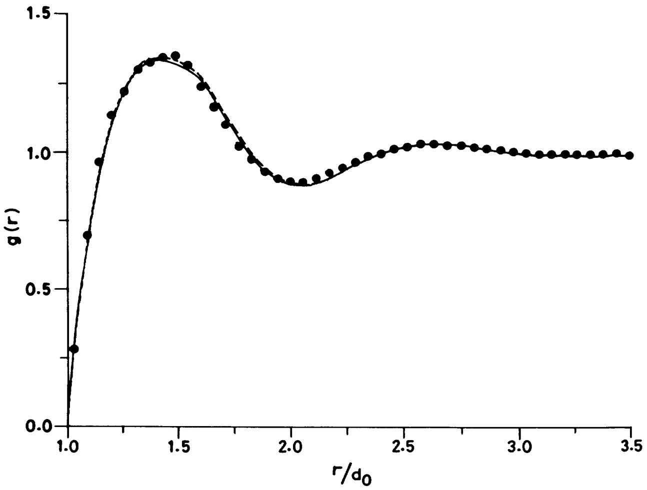

FIG. 1. Pair correlation function of the center of mass $g(r)$ for $x_0=2$, $\eta=0.3702$. The solid and dashed curves are PY results obtained with basis sets I and II, respectively. The circles are MD results of Talbot, Perera, and Patey [16].

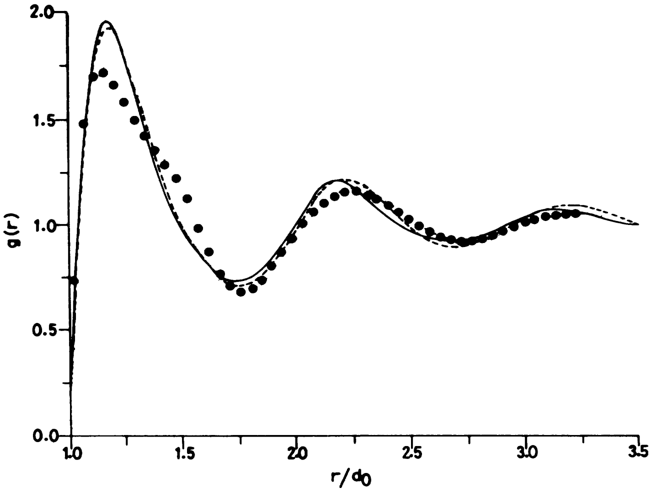

FIG. 2. Pair correlation function of the center of mass $g(r)$ for $x_0=2$, $\eta=0.592\,38$. The curves are the same as in Fig. 1.

At $\eta=0.592\,38$ for $x_0=2$ the MD results (shown in Fig. 2) exhibit a shoulder in the first peak of $g(r)$. This shoulder is not found in our PY solution. This qualitative difference in the results found by the PY approximation and the MD simulation may be due to the difference in the overlap model for HER taken in these two calculations.

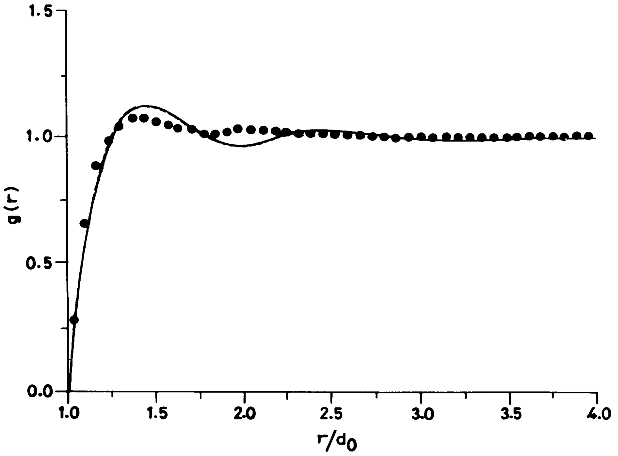

FIG. 3. Pair correlation function of the center of mass $g(r)$ for $x_0=3$, $\eta=0.3702$. The curves are the same as in Fig. 1.

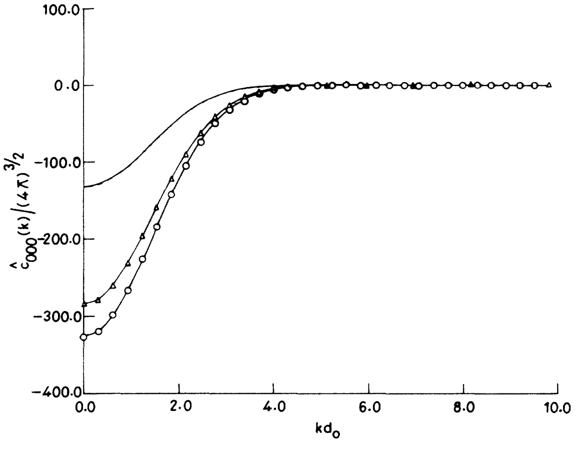

FIG. 4. The SF spherical harmonic coefficient $\hat{c}_{000}(k)/(4\pi)^{3/2}$ at $x_0=3$. The solid and dashed curves are for $\eta=0.3702$ obtained with basis sets I and II, respectively. The dashed curve is indistinguishable from the solid on the scale used in the figure. The solid curve with circles and solid curve with triangles are for $\eta=0.48$ obtained with basis sets I and II, respectively.

In Fig. 4 we plot the SF zero-angular-momentum c harmonics for both basis sets in k space for $x_0=3$ at $\eta=0.3702$ and 0.48. From this figure and also from the results of nonzero-angular-momentum harmonics we conclude that while the two sets give almost identical results for all c harmonics at lower density, they differ considerably at higher density. The difference becomes more pronounced for harmonics with a higher l index value. It seems that the basis set I overestimates the density dependence of c harmonics.

Knowledge of the coefficients of spherical harmonic expansion makes it possible to obtain detailed information on the orientational structure of the fluid. Besides a direct interpretation of the structure through the harmonic coefficients, we may examine as well the full PCF at some fixed variables. The typical specific orientations usually used are as follows: (i) parallel ($\theta_1=\theta_2=\pi/2$, $\phi_{12}=0$), (ii) T shaped ($\theta_1=\pi/2$, $\theta_2=\phi_{12}=0$), (iii) crossed ($\theta_1=\theta_2=\phi_{12}=\pi/2$), and (iv) end-to-end ($\theta_1=\theta_2=\phi_{12}=0$) configurations. There are some computer simulation results in the literature for a full PCF of spherocylinders [18] for these orientations but not for HER to the best of our knowledge.

The values of the pair distribution function obtained by forming the sum of 14 and 30 BF harmonic coefficients are shown in Figs. 5–8 for $x_0=3$ and $\eta=0.3702$. One would expect these curves to exhibit a behavior similar to that of the function $g(r)$. At a separation less than x_0 the results for the two basis sets differ considerably from each other. It seems that the results found from either basis set do not satisfy all the required features of the PCF for fixed orientations at small separations. This conclusion is derived from the fact that for a given orientation, the value of $g(r)$ must be zero inside the hard core. For example, for T-shape orientation, $g(r)$ should be zero for

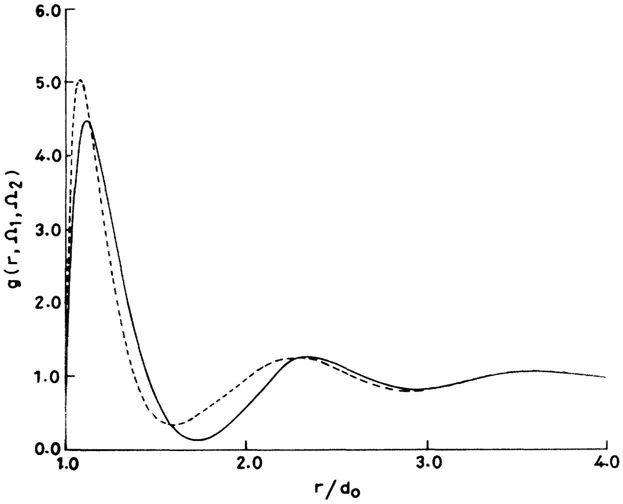

FIG. 5. Pair correlation function $g(r,\Omega_1,\Omega_2)$ for the parallel orientation for $x_0=3$, $\eta=0.3702$. The solid and dashed curves are obtained by forming the sum of 14 and 30 BF harmonic coefficients.

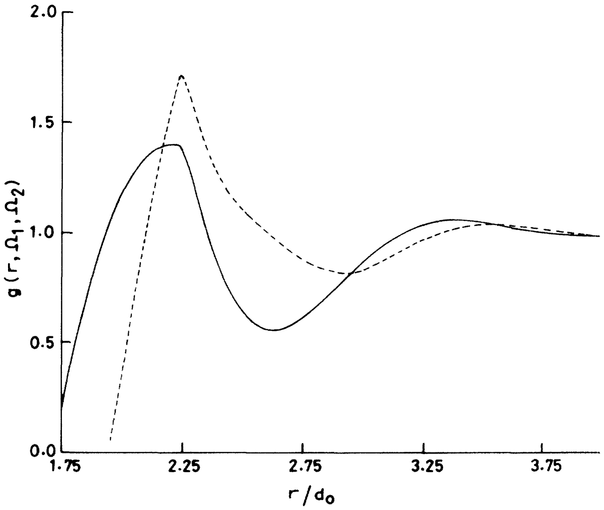

FIG. 6. Same as in Fig. 5, but for the T-shaped orientation.

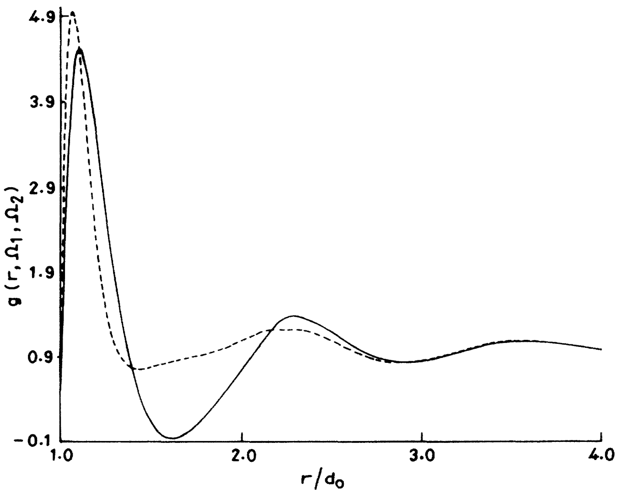

FIG. 7. Same as in Fig. 5, but for the crossed orientation.

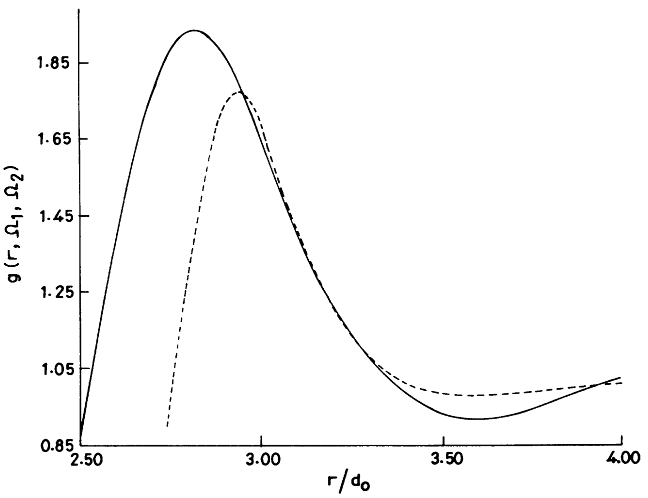

FIG. 8. Same as in Fig. 5, but for the end-to-end orientation.

$r/d_0 \leq 2$ for $x_0=3$. Viewed from this point as well as from the qualitative nature of $g(r)$ found from Monte Carlo simulations [18] for hard spherocylinders we conclude that the basis set II gives reasonable values for the PCF's. One may, however need more harmonics if one wants to consider the system at higher densities or higher values of x_0.

In Fig. 9 we plot the values of DPCF obtained by forming a sum of 30 BF harmonic coefficients as a function of r/d_0 for $x_0=3$ and $\eta=0.3702$ for all four specific orientations discussed above. The results do not appear to satisfy all the required features of the DPCF for fixed orientations for $1 \leq r/d_0 \leq x_0$. We note that the convergence in the region close to $r/d_0 \sim 1$ is very slow. The oscillations found in the values of DPCF in this region are most probably due to truncation. It seems that many more harmonics will be needed to have proper convergence. Since in most applications we need the moments of the DPCF's, the error arising due to the truncation may not seriously affect the result.

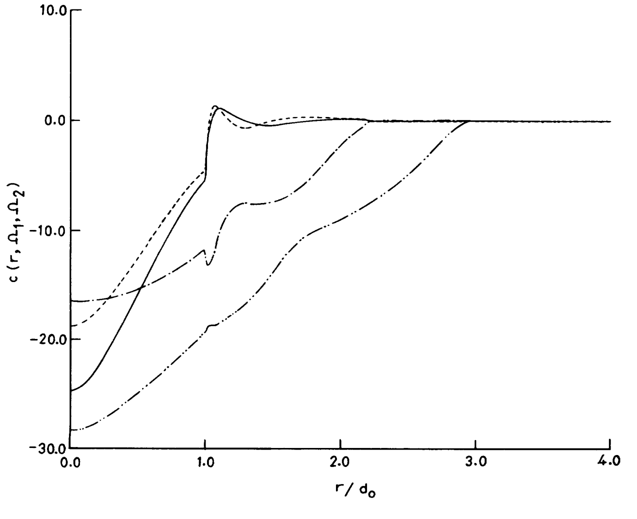

FIG. 9. Direct pair correlation function $c(r,\Omega_1,\Omega_2)$ for $x_0=3$, $\eta=0.3702$. The solid line is for parallel orientation; the dashed line for crossed orientation; and the dashed-dotted and dashed-double-dotted lines for T-shaped and end-to-end orientations, respectively.

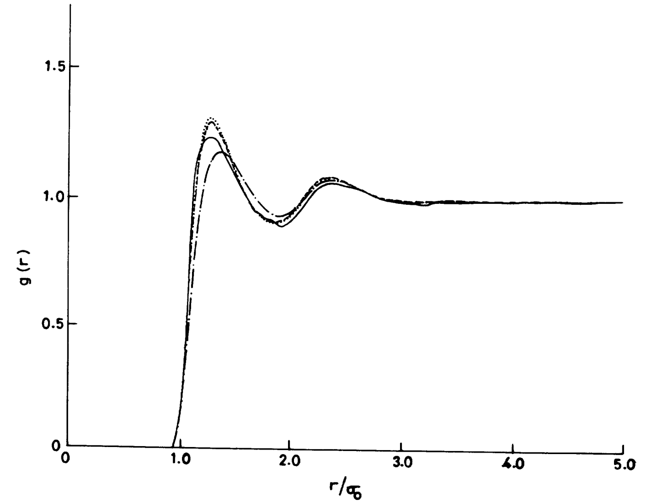

FIG. 10. Pair correlation function of the center of mass $g(r)$ for $x_0=3$, $k'=5$, $T^*=1.25$, and $\eta=0.44$. The solid line is the MD result of Miguel and co-workers (Ref. [9]). The dashed and the dotted curves are PY results obtained with basis sets I and II, respectively. The dash-dot curve is the PCF of the GB fluid in zeroth-order approximation.

B. GB fluid

We have solved the PY equation for the GB fluid for $x_0=3$ and well depth ratio $k'=5$. In Figs. 10 and 11, we compare the values of $g(r)=1+h_{000}(r)/4\pi$ for the two basis sets with each other and with the MD results of Miguel and co-workers [9] at reduced temperatures $T^*(=kT/\epsilon_0)=1.25$ and at densities $\eta=0.44$ and 0.534 07, respectively. Here the MD results are shown by a full line. From these figures the following observations

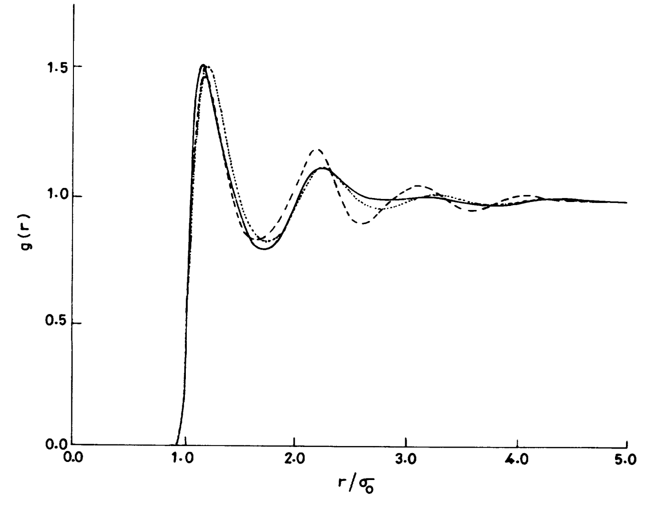

FIG. 11. Same as in Fig. 10 but for the $x_0=3$, $k'=5$, $T^*=1.25$, and $\eta=0.534\,07$.

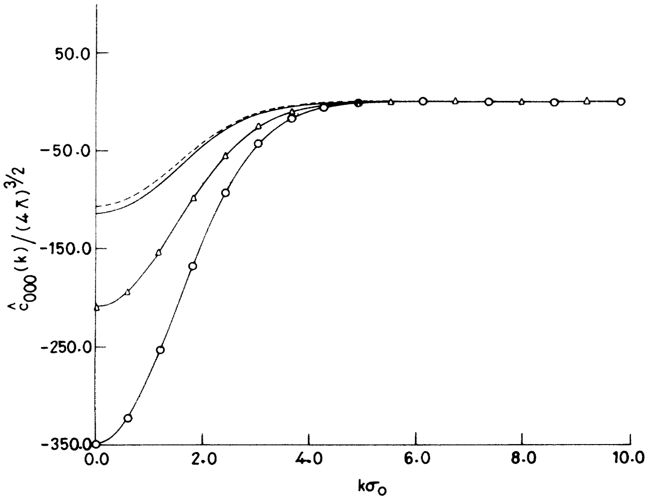

FIG. 12. The SF spherical harmonic coefficient $\hat{c}_{000}(k)/(4\pi)^{3/2}$ for the GB fluid at $x_0=3$, $k'=5$, $T^*=1.25$. The solid and dashed curves are for $\eta=0.44$ obtained with basis sets I and II, respectively. The solid curve with circles and solid curve with triangles are for $\eta=0.534\,07$ obtained with basis sets I and II, respectively.

can be made: (i) At high density, i.e., at $\eta=0.534\,07$ the basis set I gives values of $g(r)$, which have more pronounced second and higher peaks than the results of basis set II and the MD values; (ii) the maxima of the first peak for the basis set II is shifted slightly to the larger value of r/σ_0 than the MD and the basis set I results; (iii) the overall agreement between the simulation values and the values of the basis set II is satisfactory; and (iv) at density $\eta=0.44$ the results of both basis sets are in close agreement, but appear to overestimate the first peak of $g(r)$. Since computer simulation results are not available for other harmonics of PCF's we do not plot them here.

In Fig. 12 we compare the value of $\hat{c}_{000}(k)$ found from the two basis sets at $T^*=1.25$ and at two densities $\eta=0.44$ and $0.534\,07$. While the results of the two basis sets are close for $\eta=0.44$, they differ considerably for $\eta=0.534\,07$. This trend is also observed for the nonzero-angular-momentum c harmonics. As in the case of the HER model, the basis set I appears to overestimate the density dependence of c harmonics. The difference between the results of the two basis sets is found to increase for harmonics with a higher l index.

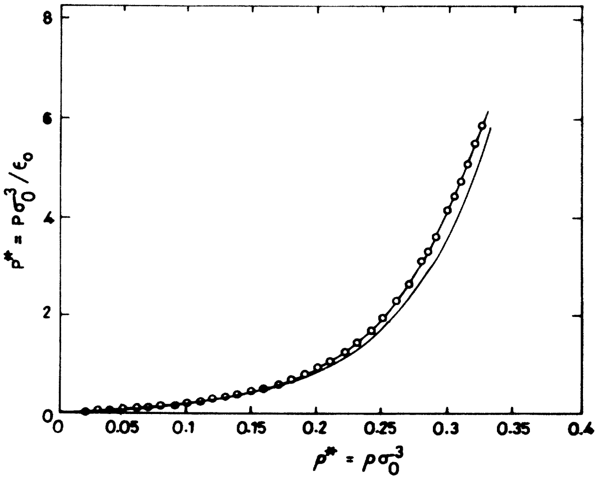

FIG. 13. Pressure as a function of fluid density for the GB fluid for $x_0=3$, $k'=5$, and $T^*=1.25$. The solid curve is the present PY result obtained using the compressibility equation. The open circles are the MD result of Miguel and co-workers.

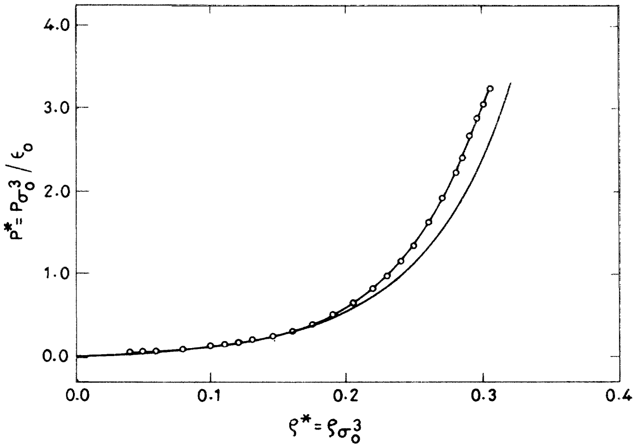

FIG. 14. Same as in Fig. 13, but for $x_0=3$, $k'=5$, and $T^*=0.95$.

In Figs. 13 and 14 we compare the pressure versus density derived from the direct PCF compressibility sum rule obtained from using basis set II to MD simulation results [9] for $x_0=3$, $k'=5$ at $T^*=1.25$, and 0.95, respectively. The PY theory appears to underestimate the pressure of the fluid at a given density at both temperatures. This feature has also been found in the case of the Lennard-Jones (12-6) potential model. It seems that the PY theory underestimates the value of $\hat{c}_{000}(0)$, which appears in the compressibility equation.

In Fig. 10 we have plotted values of $g(r)$ found from Eq. (3.5) which, in the zeroth-order approximation, give the PCF of the GB fluid. To get this results we have first solved Eq. (3.10) to find the value of d_0^* as a function of density and temperature. In Table II we give the values of d_0^* at a few densities and temperatures. As expected, the value of d_0^* is found to decrease as the temperature and density are increased. Once d_0^* is known, the value of PCF can be calculated in the said approximations us-

TABLE II. The distance of the minor axis of an effective hard ellipsoid (d_0^*) at $x_0=3$ and $k'=5$ for the reference part of the Gay-Berne potential.

T^*	η	d_0^*
1.25	0.3702	0.990 306
	0.4400	0.989 997
	0.4800	0.989 774
0.95	0.3702	0.997 234
	0.4400	0.997 037
	0.4800	0.996 889

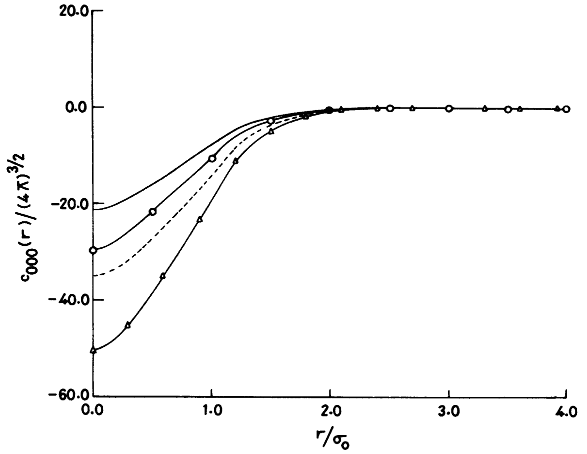

FIG. 15. The SF spherical harmonic coefficient $c_{000}(r)/(4\pi)^{3/2}$ for the GB fluid at $x_0=3$, $k'=5$, and $T^*=1.25$ obtained with basis set II. The solid curve and solid curve with circles are the PY results for the full GB model at $\eta=0.44$ and 0.48, respectively. The dashed and solid curve with triangles are the perturbation theory results at $\eta=0.44$ and 0.48, respectively.

ing Eqs. (3.5) and (3.6). For this we have used results of HER of basis set II. From Fig. 10 we find that the results found for the center of mass PCF from Eq. (3.5) underestimates the first peak and oscillates out of phase with the MD and PY results. In Fig. 15 we compare SF zero-angular-momentum c harmonics found from the PY equation and from Eq. (3.6) for $x_0=3$ at $T^*=1.25$ and $\eta=0.44$ and 0.48. We see that the perturbation theory gives values of c harmonics which qualitatively agree with the PY results but are more negative at small r than the PY results for all harmonics.

V. SUMMARY AND CONCLUSIONS

For fluids of axially symmetric nonspherical molecules the angle-dependent PCF's are expanded in products of spherical harmonics either in a BF or SF coordinate frame. The expansion coefficients of these two frames are related through a linear transformation [see Eq. (2.5)]. In this paper we solved numerically the OZ equation using the PY closure relation to obtain values of these expansion coefficients. We reported results for a model fluid of HER and for a fluid the molecules of which interact via the GB pair potential model. The reason for considering these fluids is that the corresponding models of hard spheres and the Lennard-Jones (12-6) of atomic systems have played a very important role in understanding the structure, thermodynamics, and freezing of systems of spherically symmetric molecules. The computer simulation results have already indicated that the two fluids studied here capture some properties of real liquid crystal systems [8–10].

In a numerical calculation, one has to truncate the expansion series and solve the OZ equation with only a finite number of the harmonic coefficients. The convergence of the series depends on the values of x_0 and ρ_f. For both systems we have examined the convergence of the expansion series and found that for $x_0 \leq 3$ one gets good results at all fluid densities if one considers all terms of the basis set II given in Table I. Our results also show that the values of h- and c-harmonic coefficients which involve the l index close to the truncated value may be in some error due to the truncation. Since most of the properties of interest of a given system are expressed in terms of the harmonic coefficients having l index 0 or 2 we expect that the results found from the basis set II should be satisfactory even for $x_0 > 3$.

From the results given above, it seems that the PY closure relation gives values of the harmonic coefficients, which are in good qualitative agreement with the computer simulation results. The quantitative agreement is, however, not very satisfactory particularly for the higher-order harmonic coefficients. For the GB potential the pressure calculated through the compressibility routes is found to be underestimated. We may recall that the PY theory gives similar results for the Lennard-Jones (12-6) fluid [19]. For fluids of HER it has, however, been reported [17] that the PY virial and the HNC compressibility equations give very similar and reasonably accurate results for the equation of state. Further, the PY theory is believed to underestimate the angle-dependent part of the PCF's while the HNC theory overestimates them. These theories are not thermodynamically consistent. This motivated many workers to propose different closure relations, which are thermodynamically consistent [20]. However, all such calculations are so far limited to atomic systems. Their extension to molecular system is desirable.

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