

Thermodynamically self-consistent integral-equation theory for pair-correlation functions of a molecular fluid

Ram Chandra Singh, Jokhan Ram, and Yashwant Singh

Department of Physics, Banaras Hindu University, Varanasi 221 005, India

(Received 10 October 1995)

We propose a ‘‘mixed’’ integral equation for the pair correlation function of molecular fluids which interpolates between the hypernetted-chain and Percus-Yevick approximations. Thermodynamic consistency between the virial and compressibility equation of state is achieved by varying a single parameter in a suitably chosen mixing function. The integral equation proposed here generalizes the suggestion by Rogers and Young [Phys. Rev. A **30**, 999 (1984)] to an angle-dependent pair potential. When compared to available computer simulation data, the equation is found to yield excellent results for both the thermodynamic properties and the pair-correlation functions. [S1063-651X(96)02507-X]

PACS number(s): 61.20.Gy, 61.25.Em

The pair-correlation functions (PCF's) of molecular fluids are the lowest order microscopic quantities which, on one hand, contain information about the structure of the fluid and, on the other, have direct contact with the underlying intermolecular interactions [1,2]. The values of these correlations as a function of intermolecular separations and orientations at a given temperature and pressure are found either by computer simulations or by semianalytic approximate methods [3]. In the latter approach one solves the Ornstein-Zernike (OZ) equation,

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

where 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's, with suitable closure relations such as the Percus-Yevick (PY) equation, hypernetted chain (HNC) equation, mean spherical approximation (MSA), etc. Approximations are introduced in the theory through these closure relations. In Eq. (1), $i \equiv x_i$ denotes both the location r_i of the center of the i th molecule and its relative orientation Ω_i , described by the Euler angles θ , ϕ , and ψ .

Compared to atomic fluids for which solutions to the OZ equation have been obtained for a variety of pair potentials over wide ranges of temperature and density, our knowledge of the correlation functions of the fluid of nonspherical molecules is meager [4]. In recent years numerical methods have, however, been developed to solve the OZ equation with the PY and HNC closure relations for nonspherical molecules of fixed geometry. Patey and co-workers [5] have solved both the HNC and PY equations for systems of hard ellipsoids of revolutions (HER), hard spherocylinders (HSC) and for model fluids characterized by the pair potential of a generalized Maier-Saupe type. Ram, Singh, and Singh [4] have solved the PY equation for HER and for the Gay-Berne potential [6]. Though the results found for these model potentials are in qualitative agreement with computer simulation results [4,5,7], the quantitative agreements are not satisfactory. Moreover, these theories, as for the case of atomic

fluids, are thermodynamically inconsistent, i.e., the pressure obtained from the virial and compressibility routes have different values.

In this communication we extend the method of Rogers and Young [8] and impose thermodynamic consistency on the solutions for molecular fluids by modifying the closure relation with a formula which contains an adjustable parameter and then by varying this parameter until consistency is achieved. We show the suitability of this method for a fluid of HER. The potential energy of the interaction of a pair of HER is represented as

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

where $D(\hat{r}_{12}, \Omega_1, \Omega_2)$ is the distance of closest approach of two molecules with orientations Ω_1 and Ω_2 in a direction given by \hat{r}_{12} . For $D(\hat{r}_{12}, \Omega_1, \Omega_2)$ we use the expression given by the Gaussian overlap model of Berne and Pechukas [9].

The PY and HNC integral equation theories are given by the OZ equation coupled with the closure relation

$$c^{\text{PY}}(1,2) = f(1,2) [1 + \gamma(1,2)], \quad (3a)$$

and

$$c^{\text{HNC}}(1,2) = h(1,2) - \ln[1 + h(1,2)] - \beta u(1,2), \quad (3b)$$

respectively. Here $f(1,2) = \exp[-\beta u(1,2)] - 1$, and $\beta = (k_B T)^{-1}$. We find it convenient to separate the overlap and nonoverlap regions and choose

$$c(1,2) = \begin{cases} -1 - \gamma(1,2) & \text{for overlap region,} \\ c^{\text{CL}}(1,2) & \text{for nonoverlap region.} \end{cases} \quad (4a) \quad (4b)$$

Since in the overlap region $1 + h(1,2) = g(1,2)$ is zero, Eq. (4a) is exact. For $c^{\text{CL}}(1,2)$ one uses a closure relation given by Eq. (3) or any other form.

In order to reduce and solve Eq. (1) with a closure relation it is convenient to expand all angle-dependent functions in

spherical harmonics either in a space-fixed (SF) frame or in a body-fixed (BF) frame. For example, the expansion of the direct PCF in a BF frame is written as

$$\begin{aligned} c(1,2) &= c(r_{12}, \Omega_1, \Omega_2) \\ &= \sum_{i_1 i_2 m} c_{i_1 i_2 m}(r_{12}) Y_{i_1 m}(\Omega_1) Y_{i_2 m}(\Omega_2), \end{aligned} \quad (5a)$$

where $\underline{m} = -\underline{m}$, the coefficients $c_{i_1 i_2 m}(r_{12})$ are defined by

$$c_{i_1 i_2 m}(r_{12}) = \int c(r_{12}, \Omega_1, \Omega_2) Y_{i_1 m}^*(\Omega_1) Y_{i_2 m}^*(\Omega_2) d\Omega_1 d\Omega_2. \quad (5b)$$

For fixed r_{12} , we can split the integral in Eq. (5b) into two parts corresponding to the regions of orientational space where the particles do and do not overlap. Thus we have

$$\begin{aligned} c_{i_1 i_2 m}(r_{12}) &= \int_{\text{OV}} c(r_{12}, \Omega_1, \Omega_2) Y_{i_1 m}^*(\Omega_1) Y_{i_2 m}^*(\Omega_2) d\Omega_1 d\Omega_2 \\ &\quad + \int_{\text{NOV}} c(r_{12}, \Omega_1, \Omega_2) Y_{i_1 m}^*(\Omega_1) \\ &\quad \times Y_{i_2 m}^*(\Omega_2) d\Omega_1 d\Omega_2, \end{aligned} \quad (6)$$

where OV denotes the overlap and NOV in the nonoverlap regions. Applying the relations (4) and using the orthonormal properties of the spherical harmonics, Eq. (6) can be expressed in simple form

$$\begin{aligned} c_{i_1 i_2 m}(r_{12}) &= \sum_{i_1' i_2' m'} [-4\pi \delta_{000}^{i_1' i_2' m'} - \gamma_{i_1' i_2' m'}(r_{12}) \\ &\quad - c_{i_1' i_2' m'}^{\text{CL}}(r_{12})] A_{i_1 i_2 m}^{i_1' i_2' m'}(r_{12}) + c_{i_1 i_2 m}^{\text{CL}}(r_{12}), \end{aligned} \quad (7)$$

where

$$\begin{aligned} A_{i_1 i_2 m}^{i_1' i_2' m'}(r_{12}) &= -\frac{1}{4\pi} \sum_{LL'M} \left[\frac{(2i_1+1)(2i_1'+1)(2i_2+1)(2i_2'+1)}{(2L+1)(2L'+1)} \right]^{1/2} \\ &\quad \times C_g(i_1 i_1' L; \underline{m} \underline{m}' M) C_g(i_2 i_2' L'; \underline{m} \underline{m}' M) f_{LL'M}(r_{12}). \end{aligned} \quad (8)$$

Here $C_g(i_1 i_2 i; m_1 m_2 m)$ are the Clebsch-Gordon coefficients.

In actual applications $c_{i_1 i_2 m}^{\text{PY}}(r_{12})$ used in Eq. (7) are obtained from the expansion given in our earlier paper [4] and for $c_{i_1 i_2 m}^{\text{HNC}}(r_{12})$ for HER in [10]

$$\begin{aligned} c_{i_1 i_2 m}^{\text{HNC}}(r_{12}) &= \sum_{i_1', i_1'', i_2', i_2''} \frac{1}{4\pi} \left[\frac{(2i_1'+1)(2i_1''+1)(2i_2'+1)(2i_2''+1)}{(2i_1+1)(2i_2+1)} \right]^{1/2} \\ &\quad \times \sum_{m', m''} C_g(i_1' i_1'' i_1; m' m'' m) C_g(i_2' i_2'' i_2; \underline{m}' \underline{m}'' \underline{m}) \int_{r_{12}}^{\infty} h_{i_1' i_2' m'}(r_{12}') \frac{\partial}{\partial r_{12}'} [-\gamma_{i_1' i_2' m'}(r_{12}')] dr_{12}'. \end{aligned} \quad (9)$$

To achieve thermodynamic consistency we use a closure relation

$$c_{i_1 i_2 m}^{\text{CL}}(r_{12}) = s(r_{12}) c_{i_1 i_2 m}^{\text{HNC}}(r_{12}) + [1 - s(r_{12})] c_{i_1 i_2 m}^{\text{PY}}(r_{12}), \quad (10)$$

where

$$s(r_{12}) = 1 - e^{-\alpha r_{12}}.$$

Here α , an adjustable parameter, is used to achieve thermodynamic consistency. In writing Eq. (10) it is assumed that the error introduced in the values of the PCF's by the PY and HNC closures are of the same nature for all harmonic coefficients and that the exact values lie in between the values given by these two theories. These appear to be reasonable assumptions, at least for the fluid of HER for which detailed comparison between the results found from the PY and HNC theories with the computer simulation results are available

[5]. Hereinafter we refer to the closure relation of Eq. (10) as the thermodynamically consistent (TC) relation.

The numerical methods used to solve Eq. (1) with the closure relation is the same as described in our earlier paper [4]. The number of terms included in the rotational invariant expansion of the correlation function is the same as given by set II of Table I of Ref. [4]. Here we report the results for a fluid of HER. A state of a HER fluid is defined by the packing fraction $\eta = (\pi/6) \rho_f^* x_0$, where $x_0 = 2a/2b$, $2a$ being the major axis and $2b (= d_0)$ the minor axis of an ellipsoid and $\rho_f^* = \rho_f d_0^3$. All numerical calculations have been carried out using $M=1024$ grid points with grid width $\Delta r = 0.01$, the step size in Fourier space being $\Delta k = \pi/M \Delta r$. All one dimensional integrals are evaluated using the trapezoidal rule. The solution of the PY, HNC, and TC equations have been obtained at several densities and at a different consistency parameter for $x_0 = 1.0, 2.0$ and 3.0 .

Once the PCF's are known, they can be used to calculate pressure from the virial and compressibility equations in a

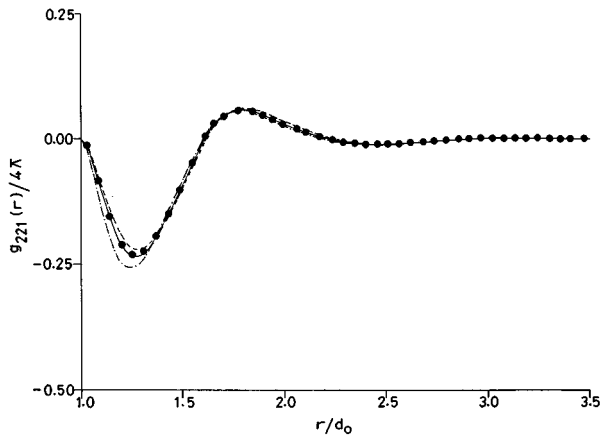


FIG. 1. The spherical harmonic coefficient $g_{221}(r)/4\pi$ in the body-fixed frame for $x_0=2.0$, $\eta=0.3702$. The solid, dashed, dash-dotted curves are, respectively, TC, PY, and HNC results. The solid circles are MD results of Talbot, Perera, and Patey (Ref. [5]).

straightforward way [3]. The value of α is adjusted till the value of pressure found from these two routes coincide with each other. The value of α found in this way for $x_0=1.0$, 2.0, and 3.0 are, respectively, 0.16, 0.33, and 0.50. Note that the value of α for $x_0=1.0$ which corresponds to a hard sphere, coincides with that of Rogers and Young [8]. The value of α is found to increase with x_0 which means that the HNC component in Eq. (10) increases with x_0 . This appears reasonable from the fact that as x_0 increases the ‘‘effective’’ repulsion between two ellipsoids of revolution becomes more like a repulsion between soft spheres. This softness increases with increasing x_0 . One way to visualize this is to calculate the ‘‘effective’’ potential from the angle averaged Boltzmann factor.

The kind of agreement one finds for results found from the PY, HNC, and TC theories with the computer simulation results is revealed from Figs. 1 and 2 in which $g_{221}(r)$ harmonic coefficient of the total PCF is plotted as a function of r for $x_0=2.0$ and 3.0, respectively. The TC theory gives better agreement with the simulation results. In Figs. 3 and 4 we plot pressure as a function of density for $x_0=2.0$ and 3.0, respectively. The values found from the TC relation agree

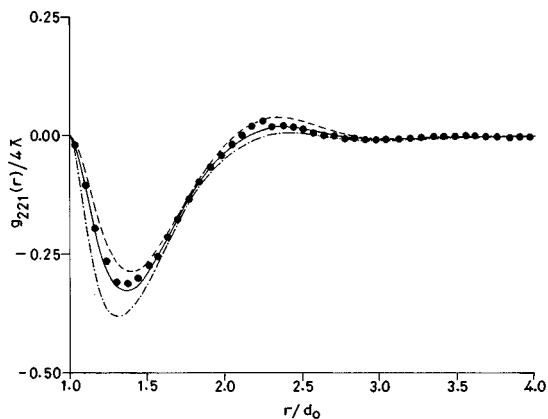


FIG. 2. The spherical harmonic coefficient $g_{221}(r)/4\pi$ in the body-fixed frame for $x_0=3.0$, $\eta=0.3702$. The curves are the same as in Fig. 1.

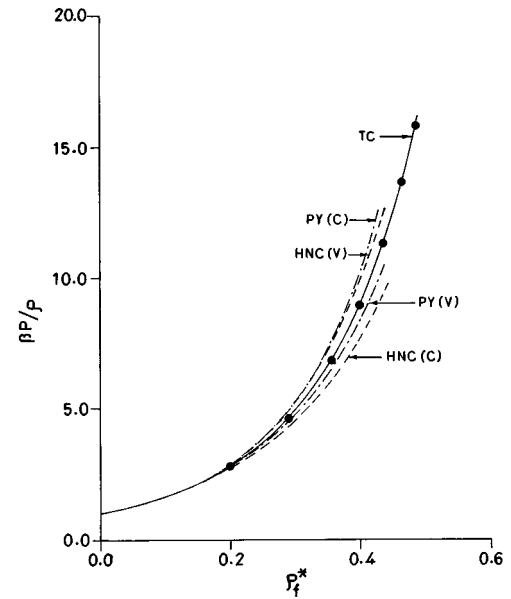


FIG. 3. Pressure as a function of fluid density for $x_0=2.0$. The solid circles represent the Monte Carlo result of Mulder and Frenkel (Ref. [11]) and the solid curve is the TC result. The dash-dotted and the dashed curves are, respectively, PY and HNC results. Here, V and C denote the virial and compressibility results, respectively.

very well with the computer simulation results of Mulder and Frenkel [11]. One may, however, note that the simulation results given in these figures are for the exact HER overlap which is not identical to the Gaussian model used by us. It may therefore be possible that the results found for the Gaussian model may not equally match with the simulation results for all the harmonic coefficients of the PCF’s. Furthermore, the value of α needed to achieve self-consistency for the exact HER overlap may also differ from those reported here. But these observations do not change the conclusions reached here.

In a theory of freezing of molecular liquids into a nematic phase the structural parameter $\hat{c}_{i_1 i_2}^{(0)}$ defined as [12]

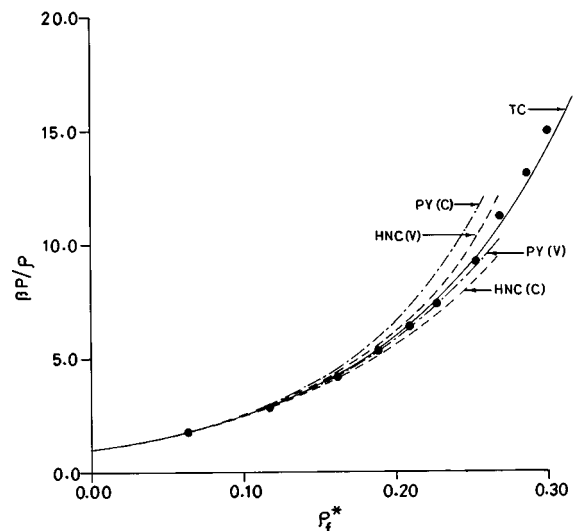


FIG. 4. Pressure as a function of fluid density for $x_0=3.0$. The curves are the same as in Fig. 3.

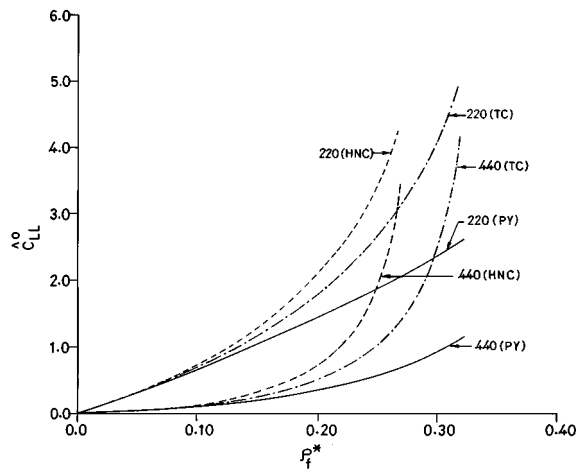


FIG. 5. The structural parameter $\hat{c}_{LL}^{(0)}$ at $x_0=3.0$. The solid, the dash, and the dash-dotted curves are, respectively, PY, HNC, and TC results.

$$\hat{c}_{i_1 i_2}^{(0)} = (2i_1 + 1)(2i_2 + 1) \rho_f \int d\mathbf{r} d\Omega_1 d\Omega_2 c(r, \Omega_1, \Omega_2) \times P_{i_1}(\cos\theta_1) P_{i_2}(\cos\theta_2)$$

plays an important role. Here P_i is a Legendre polynomial of degree i and angles refer to a space-fixed z axis. Note that

$\hat{c}_{00}^{(0)}$ is related to the isothermal compressibility and $\hat{c}_{22}^{(0)}$ and the higher-order coefficient to the freezing parameters. The quantity $\hat{c}_{22}^{(0)}$ and $\hat{c}_{44}^{(0)}$ are found to be very sensitive to the approximations involved in a given integral equation theory. In Fig. 5 we compare the values of the structural parameters $\hat{c}_{22}^{(0)}$ and $\hat{c}_{44}^{(0)}$ found from these theories for $x_0=3.0$. The PY theory is believed to underestimate the angle-dependent part of the PCF's while the HNC theory overestimates them. This is seen from the general instability condition for isotropic liquid which is derived from the Kerr constant [13] and is written as

$$1 - \frac{1}{5} \hat{c}_{22}^{(0)} \leq 0.$$

The HNC theory predicts that the isotropic fluid of HER will be unstable for $\eta \geq 0.435$ while for TC theory this is for $\eta \geq 0.50$ which is close to the isotropic-nematic transition packing fraction [11]. For PY theory it is found that the isotropic phase remains stable even at very high densities.

In conclusion we wish to emphasize that the thermodynamically self-consistent theory proposed here provides accurate values of both the pair-correlation functions and thermodynamic properties of molecular fluids.

We thank the Department of Science and Technology, New Delhi for financial assistance through a research grant.

- [1] J. A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**, 587 (1976).
 [2] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1976).
 [3] C. G. Gray and K. E. Gubbins, *Theory of Molecular Fluids* (Clarendon, Oxford, 1984).
 [4] J. Ram, R. C. Singh, and Y. Singh, *Phys. Rev. E* **49**, 5117 (1994).
 [5] A. Perera, P. G. Kusalik, and G. N. Patey, *J. Chem. Phys.* **87**, 1295 (1987); J. Talbot, A. Perera, and G. N. Patey, *Mol. Phys.* **70**, 285 (1990).

- [6] J. G. Gay and G. J. Berne, *J. Chem. Phys.* **74**, 3316 (1981).
 [7] E. D. Miguel, L. F. Rull, M. K. Chalam, K. E. Gubbins, and E. V. Swol, *Mol. Phys.* **72**, 593 (1991); E. D. Miguel, L. F. Rull, M. K. Chalam, and K. E. Gubbins, *ibid.* **74**, 405 (1991).
 [8] F. J. Rogers and D. A. Young, *Phys. Rev. A* **30**, 999 (1984).
 [9] B. J. Berne and P. Pechukas, *J. Chem. Phys.* **56**, 4213 (1972).
 [10] P. H. Fries and G. N. Patey, *J. Chem. Phys.* **82**, 429 (1985).
 [11] D. Frenkel, B. Mulder, and J. P. McTague, *Phys. Rev. Lett.* **52**, 287 (1984); B. Mulder and D. Frenkel, *Mol. Phys.* **55**, 1193 (1985).
 [12] Y. Singh, *Phys. Rep.* **207**, 351 (1991).
 [13] J. C. Filippini and Y. Poggi, *J. Phys. Lett.* **35**, 99 (1974).