

Pair correlation function for the hard ellipsoids under decoupling approximation

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Abstract : Pair correlation functions have been calculated using decoupling approximation under Percus Yevick approximation by employing spherical harmonics coefficients and a potential model suggested by Singh and Singh [*Phys. Rev.* B33 2725 (1986)] for the hard ellipsoids. It has been reported that the decoupling approximation compares well with Monte Carlo results of Nezbeda only at lower values of packing fraction and parametric ratio of length-to-breadth.

Keywords : Pair correlation function, hard ellipsoids, decoupling approximation.

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1. Introduction

Matter usually exists either as a dense solid or as a dilute vapor at low pressure. A third state of matter appears at higher pressure is the liquid state [1]. Liquids are of two types viz., (a) atomic or simple liquids in which intermolecular potential energy between molecules depends only on the intermolecular distance R_{ij} e.g., alkali metals and certain molten salts. The atomic liquids are also inert gases where two molecules do not interact with each other and the liquids are made up of atoms only, and (b) molecular liquids in which intermolecular potential energy depends not only on their intermolecular distances but also depends on the molecular orientation, vibrational coordinates, etc. e.g., N_2 , CO_2 , CCl_4 , C_6H_6 , etc. [2,3].

In the rigid molecular approximation [4,5], intermolecular potential energy $U(R_{ij}, \Omega_i, \Omega_j)$ for a pair of molecules depends on the vector $R \equiv (R, \theta, \phi)$ from center of molecules i to center of molecules j and on orientations Ω_i and Ω_j of the molecules relative to some space fixed set of axes. For the linear molecules (e.g., CO_2 , N_2 , HCl , etc.), $\Omega_i \equiv (\theta_i, \phi_i)$, where θ_i, ϕ_i are the usual polar angles and

for the nonlinear molecules (e.g., H_2O , CCl_4 , etc.), $\Omega_i \equiv (\theta_i, \phi_i, \chi_i)$, where θ_i, ϕ_i, χ_i are the Euler angles. Thus, structural study of molecular liquid is very complex compared to simple liquids. Several approximations are in use to make its study easy. One of the efforts made by several workers [4-6] is to find an analytical solution by expanding pair correlation function (PCF) using spherical harmonics coefficients [4] and Ornstein-Zernike (OZ) equation [6]. The shape and size of pair correlation function have been used to study the structural behaviour of neutral molecules [6-11] as well as the ordered structures of suspended charged molecules [12-15].

From the survey of literatures, it is found, that the study of hard ellipsoid using decoupling approximation [7] under Percus Yevick (PY) approximation [16] has not been done so far. A potential model suggested by Singh and Singh [7] for the hard ellipsoids has been used along with the decoupling approximation to calculate PCF. The results of present calculation have been compared well with Monte Carlo (MC) results of Nezbeda [8]. It has been reported that the decoupling approximation approach of course

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under restricted conditions, is in good agreement with MC results at lower values of parametric ratio of length-to-breadth of hard ellipsoids and packing fraction.

2. Theory and calculations

System composed of hard ellipsoid of revolution is conveniently parameterized by length-to-breadth ratio $X_0 = a/b$, where $2a$ and $2b$ denote lengths of major and minor axes of ellipsoids. This model includes as limiting cases of hard spheres, hard platelets and hard needles systems. The potential energy of interaction of a pair of hard ellipsoids of revolution is represented as [7]

$$U(R_{ij}, \Omega_i, \Omega_j) = \infty, \quad R_{ij} \leq D(\Omega_{ij}); \quad (1a)$$

$$= 0, \quad R_{ij} \geq D(\Omega_{ij}); \quad (1b)$$

where $D(\Omega_{ij}) \equiv D(R_{ij}, \Omega_{ij})$ is the distance of closest approach of two molecules with the relative orientation Ω_{ij} . For $D(R_{ij})$, expression is given by the Gaussian overlap model of Berne and Pechukas [7] as

$$\begin{aligned} D(\Omega_{ij}) &= D(R_{ij}, \Omega_{ij}) \\ &= D_0 \left[\left\{ 1 - X \left[(\hat{R}_{ij} \cdot \hat{e}_i)^2 + (\hat{R}_{ij} \cdot \hat{e}_j)^2 + 2X(\hat{R}_{ij} \cdot \hat{e}_i) \right. \right. \right. \\ &\quad \left. \left. \left. \times (\hat{R}_{ij} \cdot \hat{e}_j)(\hat{e}_i \cdot \hat{e}_j) \right\} \times \left[1 - X^2(\hat{e}_i \cdot \hat{e}_j)^2 \right]^2 \right\}^{1/2}, \quad (2) \end{aligned}$$

where \hat{e}_i and \hat{e}_j are the unit vectors along symmetry axes of two interacting hard ellipsoids.

$$D_0 = 2b,$$

$$X = (X_0^2 - 1)/(X_0^2 + 1), \quad (3)$$

and \hat{R}_{ij} is a unit vector along intermolecular axis.

Ornstein-Zernike (OZ) equation for non-spherical molecules is given by [5,16]

$$\begin{aligned} h(R_{ij}, \Omega_i, \Omega_j) &= c(R_{ij}, \Omega_i, \Omega_j) \\ &+ \sum \rho_k \sigma_k^3 \int_0^\infty \langle c((R_{ij}, \Omega_i, \Omega_j)) h(R_{ij}, \Omega_i, \Omega_j) \rangle d^3 R, \quad (4) \end{aligned}$$

where $h(R_{ij}, \Omega_i, \Omega_j)$ is the total correlation function (TCF) which is related to PCF $g(R_{ij}, \Omega_i, \Omega_j)$ as

$$h(R_{ij}, \Omega_i, \Omega_j) = g(R_{ij}, \Omega_i, \Omega_j) - 1 \quad (5)$$

together with the closure relations

$$h(R_{ij}, \Omega_i, \Omega_j) = -1, \quad R_{ij} \leq D(\Omega_{ij});$$

$$c(R_{ij}, \Omega_i, \Omega_j) = -\beta U(R_{ij}, \Omega_i, \Omega_j); \quad R_{ij} \geq D(\Omega_{ij});$$

as the direct correlation function (DCF); $\beta = 1/kT$, ρ is the density of molecules and σ its diameter. Total volume fraction of molecules can be evaluated by

$$\eta = \frac{\pi}{6} \sum \rho_i \sigma_i^3. \quad (6)$$

In Rose's convention [7], the molecular pair correlation function can be written as

$$g_{11m}(R) = 4\pi \langle g(R_{ij}) Y_{1m}^-(\Omega_i) Y_{1m}(\Omega_j) \rangle \quad (7)$$

and

$$g(R_{ij}) = 4\pi \sum \sum \sum g_{11m}(R) Y_{1m}(\Omega_i) Y_{1m}(\Omega_j), \quad (8)$$

where $R \equiv |R_{ij} = R_j - R_i|$, $\bar{m} = -m$ and the sum on m runs from -1 to $+1$. We need only to note that spherical harmonics are normalized and orthogonal *i.e.*,

$$\int Y_{1m}^*(\Omega) Y_{1m'}(\Omega) d\Omega = \delta_{11} \delta_{mm'} \quad (9)$$

and that

$$Y_{1\bar{m}}(\Omega) = (-1)^m Y_{1m}^*(\Omega). \quad (10)$$

The expansion coefficients $g_{11m}(R_{ij})$ are the projection of $g(R_{ij})$ on corresponding angular functions. But

$$\begin{aligned} Y_{1m}(\theta, \phi) &= (-1)^m \{(21+1)/4\pi\}^{1/2} \{(1-m)!/(1+m)!\}^{1/2} \\ &\times P_{1m}(\cos\theta) \exp(im\phi), \quad m \geq 0 \quad (11) \end{aligned}$$

and

$$P_{1m}(x) = (1-x^2)^{m/2} (d/dx)^m P_1(x), \quad (12)$$

where P_{1m} is the Legendre polynomial coefficients.

Spherical harmonics coefficients have been evaluated in the expansion of pair correlation function $g(R_{ij}, \Omega_i, \Omega_j)$ for the hard ellipsoids using decoupling approximation. In this approximation, PCF has been approximated for the system of ellipsoidal structures using the PY approximation with hard spheres diameter D_0 replaced by the distance of the closest approach $D(R_{ij}, \Omega_i, \Omega_j)$. Thus,

$$g(R_{ij}, \Omega_i, \Omega_j) = g(R_{ij}, \delta/D(\Omega_{ij})) = g(R^*), \quad (13)$$

where

$$R^* = R_{ij}/D(\Omega_{ij}) \text{ and } g(R^*) = g_{PY}(R^*). \quad (14)$$

A computer program has been developed in FORTRAN to calculate the pair correlation function. All the calculations have been carried out in double precision on the HP-712/300 computer at Computer Center, B.H.U.

3. Results and discussion

The g_{11m} versus distance R^* curves denoted by T.H. in all figures represent the present theoretical results obtained using decoupling approximation under PY approximation for the different values of parametric ratio X_0 and packing fraction η are compared with the Monte Carlo results denoted by M.C. curve of Nezbeda [8]. The values for the input parameters X_0 and η have been taken from the work of Nezbeda [8] in order to test the accuracy of the results obtained using decoupling approximation.

Figure 1a shows the comparison between results

obtained using decoupling approximation *i.e.*, present theoretical results and MC results of g_{000} with distance R^* for the systems $(X_0, \eta) = (1.6, 0.2948)$ and $(2.0, 0.3879)$. It is observed that the height of first peak in the theoretical curve is less than that in MC curve for the system $(2.0, 0.3879)$ whereas its heights are almost equal for the system $(1.6, 0.2948)$ in both the curves. The position of the first peak height in theoretical curve shifts towards higher R^* for the system $(1.6, 0.2948)$ and it is nearly the same for the theoretical as well as MC curves for the system $(2.0, 0.3879)$. Almost no difference is found between theoretical and MC results for the position and the magnitude of depth of the curves for these systems.

The results of g_{000} with distance R^* calculated using decoupling approximation for the system $(X_0, \eta) = (1.4, 0.3142)$ and $(1.6, 0.3873)$ have been compared with MC results in Figure 1b. The shape and size of the first peak of g_{000} in theoretical curve coincide with the MC curve for the system $(1.4, 0.3142)$. But, a slight difference may be seen in the first depths in both the curves. The depth is deeper in theoretical curve than in the MC curve. A constant difference between theoretical and MC results has been observed in shape and size of the g_{000} versus R^* curves for the system $(1.6, 0.3873)$. Magnitude of the height of the first peak in theoretical g_{000} versus R^* curve is less than in MC curve while the depth in theoretical curve lies deeper than in the MC curve for this system.

The values of g_{200} calculated for the systems $(X_0, \eta) = (1.4, 0.3142)$ and $(1.6, 0.3873)$ are shown in Figure 2a along with the MC results. It may be seen clearly that the height of the first peak in g_{200} versus R^* curve in the present study is somewhat larger than the MC while its position shifts slightly towards lower values of R^* in the theoretical curve in comparison with the MC curve. The magnitude of depth in theoretical curve is less than in MC curve for the system $(1.4, 0.3142)$ and it is almost equal for the system $(1.6, 0.3873)$. The position of depth in theoretical curve is at lower values of R^* than that in the MC curve.

Figure 2b compares the present results with MC results for g_{200} of the systems $(X_0, \eta) = (1.6, 0.2948)$ and $(2.0, 0.3879)$. The difference in the first depths in both curves is found to be more in case of the system $(2.0, 0.3879)$ as compared to the system $(1.6, 0.2948)$. The positions of depths are almost constant. The first peak's heights in theoretical and MC curves are found to be equal for the system $(2.0, 0.3879)$ but the theoretical height of first peak is a little higher than MC for $(1.6, 0.2948)$. The position of

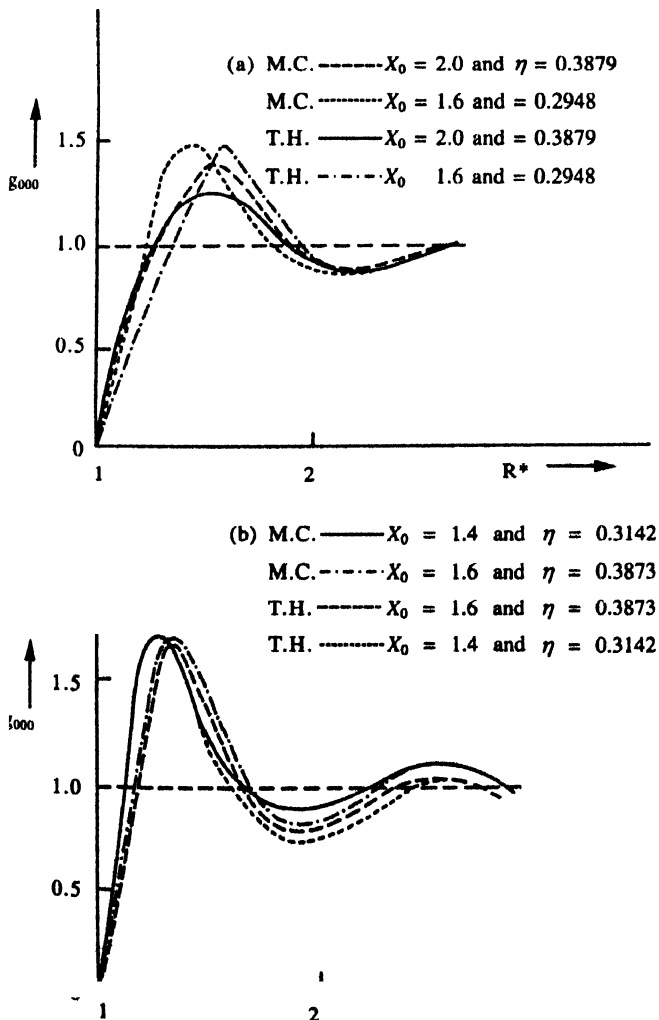


Figure 1. Variation of g_{000} with distance R^* .

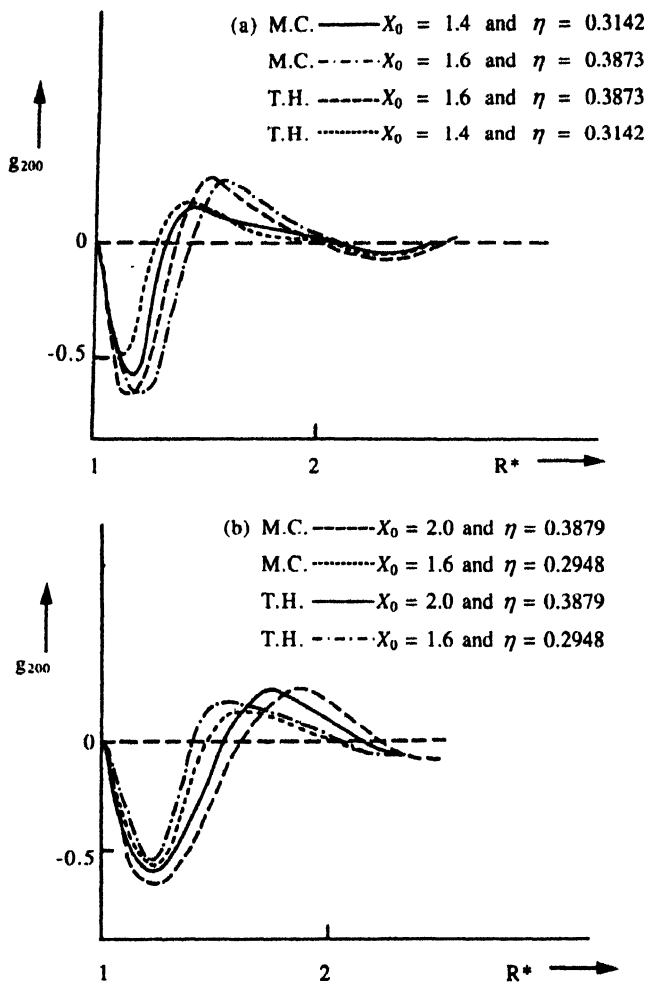


Figure 2. Variation of g_{200} with distance R^* .

the first peak in the theoretical curve lies at lower values of R^* as compared to MC curve.

The values of g_{220} obtained in the present calculation for the systems $(X_0, \eta) = (1.4, 0.3142)$ and $(1.6, 0.3873)$ are compared with the MC results in Figure 3a. The magnitudes of height of first peaks are nearly equal but position of first peak in theoretical curve shifts towards lower values of R^* . The amplitude of depth is more for MC curve and a large difference in positions of maximum depths is found between the MC and theoretical curves. The depth's position for the system $(1.6, 0.3873)$ shifts towards higher side of R^* for MC curve.

A comparison between theoretical and MC results for g_{220} is shown in Figure 3b for the systems $(X_0, \eta) = (1.6, 0.2948)$ and $(2.0, 0.3879)$. This figure clearly depicts discrepancies between theoretical and MC results for the system $(2.0, 0.3879)$ with respect to heights and positions of peaks and depths. The discrepancy is found to be less for the system of $(1.6, 0.2948)$.

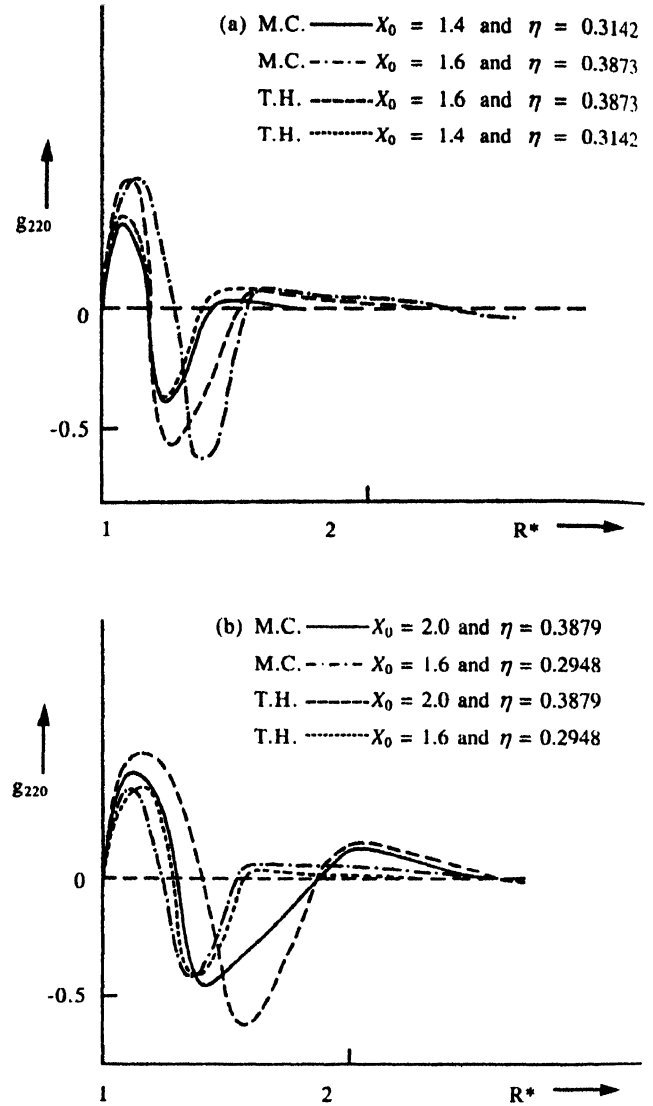


Figure 3. Variation of g_{220} with distance R^* .

4. Conclusions

Our results are in agreement with the MC results only for low X_0 and η values. However, these results overestimate the MC results for $X_0 = 2.0, \eta = 0.3879$ whereas it underestimates the MC results for $X_0 = 1.6, \eta = 0.2948$. These results show that decoupling approximation is not good enough for $X_0 > 3$. For the accurate evaluation therefore, some other approximations viz., HNC, BGY, etc may be used.

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