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Radial Distribution Function of Hard Spheres at Different Densities

A. Khanal, S. Gyawali, P. Khati, S. P. Khanal and N. P. Adhikari*
Central Department of Physics, Tribhuvan University, Kathmandu
*Corresponding Email: narayan.adhikari@cdp.tu.edu.np

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ABSTRACT

The model of hard sphere system has important part in modern theories of liquids. Hard sphere fluid is considered as the most intensively studied system among all model fluids. The thermodynamic and structural properties of real fluids can be studied with the help of hard spheres fluid. The exact solution of Ornstein-Zernike (OZ) equation with Percus-Yevick (PY) along with the equation of state provides an approximate analytical expression for radial distribution function (RDF). This work intends to study the radial distribution function of Hard sphere (HS) using the PY approximation for different densities ranging from low to high to find out their structural properties, packing behavior, phase transitions, and thermodynamics. We use FORTRAN program for this purpose. At low densities, the RDF has a single peak at a distance corresponding to the hard sphere diameter, indicating that the particles are well-separated and not interacting with each other like gaseous. As density increases, the peak becomes broader and shifts to smaller distances, indicating that the particles are coming into closer contact and interacting more strongly with each other. The height of the peak also increases, indicating that there is a greater probability of finding a particle at a certain distance from another particle.

Keywords: Hard spheres, Radial distribution function, PY approximation, Ornstein-Zernike, FORTRAN.

1. INTRODUCTION

Hard spheres (HS) fluids are considered as one of the most intensively studied system among all the model of fluids [1, 2]. The thermodynamic and structural properties of hard spheres are known to have a high degree of accuracy through the use of different computer simulations. The functional as well as analytical representation for radial distribution function (RDF or g(r)) can be achieved from the theoretical aspect. Likewise, from the practical point of view, we can obtain the graphical representation of g(r) for different range of densities and particle-particle separation [3]. The study of liquid has wide range of application in different fields such including condensed matter, biological sciences, and industries. A hard sphere is athermal (i.e. no temperature dependence). Hard spheres are defined simply as impenetrable spheres that cannot overlap in space. The hard sphere provides a generic representation that explain structure and dynamics of gaseous and liquids [4]. Hard spheres fluid is interest of model that explains useful reference system in perturbation schemes. It is studied by different means, Molecular Dynamics (MD) and by experimental study of certain colloidal model systems. It also provides a type of generic model that explains the dynamics of simple liquids [5]. Wertheim [6] used analytical solution of Percus-Yevick (PY) integral equation to obtain the theoretical result for radial distribution function (g(r)). Hard sphere is a model for fluids and solids in statistical mechanics. Hard spheres imitate the property of repulsion same as the atoms and spherical molecular encounter at very close radius. The hard sphere systems give a generic model which classifies the quasi universal structure and fluctuation of simple liquids [7]. A system of hard spheres only interacting by hard collision is a classical model fluid and is stated by the PY equation [8]. Lopez and co-workers explained that the hard spheres (HS) plays a major role in the application and use of statistical mechanics for the study of the thermodynamics as well as structural properties of the real fluids. HS fluid radial distribution function, (g(r)) was calculated by an analytical method that provides a logical extensive solution to get the PY equation with weak physical requirements. This method can be used to study the structural properties of HS mixtures in the metastable region [9]. Henderson described that the hard sphere fluid is one of the booming theory of liquids. Hard spheres interact via the hard spheres potential [10],

$$u(r) = \begin{cases} \propto; r < d \\ 0; r > d \end{cases}$$

Here, d indicates the diameter and r gives the separation of the pair of hard spheres. In the HS fluid, the Mean Spherical Approximation (MSA) and the PY Approximation are similar in nature [11]. The PY Approximation theory gives analytical solution for the direct correlation function (DCF), HS thermodynamics and the laplace transform of the radial distribution function, (RDF). Ornstein-Zernike (OZ) equation relates the direct correlation function (DCF) and radial distribution function (RDF) [12]. This OZ equation itself does not yield a theory but by combining with PY theory gives exact result for HS fluid [10]. An approximate analytical expression for the radial distribution function, (g(r)) can be obtained from the exact solution of Ornstein-Zernike (OZ) equation with Percus-Yevick (PY) equation as well as from the equation of state [9]. Nowadays, the hard sphere radial distribution function can be implemented through programming based on deterministic computation. The purpose of studying radial distribution of hard spheres at different densities is to find out their structural properties, packing behavior, phase transitions, and thermodynamics. It can also serve as a benchmark for comparing with theoretical models and validating their predictions [13]. It is possible to study the structure of a substance through the radial distribution function (RDF), which is one of its most important characteristics [14]. The radial distribution function can be defined as the probability of obtaining a particle at definite distance from an arbitrary or random central particle. It is denoted by g(r) such that "r" gives the distance between the particles [15]. An RDF for liquid displays the distribution of particles around another particle as a reference shows an oscillation until a certain distance is reached and then becomes unity. It describes the preferred position of one particle with respect to another particle [16]. The RDF unity level indicates that the atoms at this area are not correlated up to a certain distance from the reference position [17]. As the radial distribution function (RDF) of hard spheres is a measure of the probability of finding a particle at a certain distance from another particle, given that the particles are hard spheres and cannot overlap so that is commonly used in statistical mechanics to study the properties of liquids and other condensed matter systems. The RDF can be helpful to determine the thermodynamic properties and the structure of the system, such as pressure and density [18]. Additionally, it can be used to determine the pair distribution function, which can provide details about the short-range order in the system. For a variety of densities in an equilibrium fluid, and also for the metastability region, molecular dynamics simulations have been carried out on the radial distribution function of hard spheres fluids [19]. In order to study the asymptotic and short-range terms of the PY solution, it follows that g(r) can be predicted to achieve accuracy in the area of the nearest neighbors, where "r" is the position of the first minimum [3]. The code for generating g(r) numerically was provided by Perram [20]. Later on, this method was again developed by Chang and co-workers [21].

2. METHODOLOGY

P-Y approximation was defined first by Percus and Yevick in 1958 [22]. This approximation is used in solving the Ornstein-Zernike (OZ) equation as the approximation itself is a closure relation. This approximation method is also assigned as the Percus-Yevick equation [23]. To acquire the expression for the radial distribution function, g(r) this approximation can be frequently applied in the fluid theory. The radial distribution function, g(r) of the HS fluid in the range of densities $0.2 \leq \rho\sigma^3 \leq 0.9$ can be expressed as [3],

$$g(r) = 0 \text{ for } r < \sigma \quad \text{......(1)}$$

$$g(r) = \frac{A}{r} e^{\mu[r-\sigma]} + \frac{B}{r} cos(\beta[r-\sigma] + \gamma)\, e^{\alpha[r-\sigma]} \text{ for } \sigma \leq r \leq r^* \quad \text{......(2)}$$

$$g(r) = 1 + \frac{C}{r} cos(\omega r + \delta) e^{-\kappa r} \text{ for } r \geq r^* \quad \text{......(3)}$$

Here, c(r) indicates direct correlation function (DCF), ρ denotes number density and σ is the radius of hard spheres. Above equation carry two unknown parameters i.e, $\gamma(r)$ and $c(r)$. A closure relation represents that there is not all parameters that is unknown in the equation of RDF, g(r) are independent to each other. In this case, the parameters A and B of the depletion region of g(r) are uniquely represented as α, β, γ, μ and the position of the first minimum $r^* = r_m$, the minimum value g_m, and the known contact value, g_σ^{expt} can be expressed as follows [3],

$$A = \sigma g_\sigma^{expt} - B cos\gamma \quad \text{...(4)}$$

$$B = \frac{g_m - \left(\sigma \frac{g_\sigma^{expt}}{r^*}\right) exp\mu[r^* - \sigma] r^*}{cos(\beta[r^* - \sigma] + \gamma)\ exp\alpha[r^* - \sigma] - cos\gamma\ exp\mu[r^* - \sigma]} \quad \text{....(5)}$$

$$C = \frac{r^*[g_m - 1]\ exp\kappa r^*}{cos\ (\omega r^* + \delta)} \quad \text{...(6)}$$

Where, $\delta = -\omega r^* - arctan\frac{\kappa r^*}{\omega r^*}$

Also, we have

$$g_\sigma^{expt} = \frac{1}{4\eta}\left[\frac{1 + \eta + \eta^2 - \frac{2}{3\eta^3} - \frac{2}{3\eta^4}}{(1-\eta)^3} - 1\right] \quad \text{......................(7)}$$

From the comparison of hard sphere problem with monte carlo and the density functional theory (DFT), the parameters w_0 and κ_0 can be expressed as [24]

$$\omega\sigma = -0.682exp(-24.697\eta) + 4.720 + 4.450\eta \quad \text{......(8)}$$

$$\kappa\sigma = 4.674exp(-3.935\eta) + 3.536exp\ (-56.270\eta) \quad \text{......(9)}$$

Also,

$$\alpha\sigma = 44.554 + 79.868\eta + 116.432\eta^2 - 44.652(2\eta) \quad \text{......(10)}$$

$$\beta\sigma = -5.022 + 5.857\eta + 5.089\ exp(-4\eta) \quad \text{......(11)}$$

Original Wertheim solution gives the value of parameters μ_0 and ω_0 as [6]

$$\mu\sigma = \frac{2\eta}{1-\eta}\left(-1 - \frac{d}{2\eta} - \frac{\eta}{d}\right) \quad \text{......(12)}$$

$$\gamma = \text{arctan}\left\{-\frac{\sigma}{\beta_0}[(\alpha_0\sigma(\alpha_0^2 + \beta_0^2) - \mu_0\sigma(\alpha_0^2 + \beta_0^2)) \times \left(1 + \frac{1}{2}\eta\right) + (\alpha_0^2 + \beta_0^2 - \mu_0\alpha_0)(1 + 2\eta)]\right\} \quad \text{......(13)}$$

We have,

$$\frac{r^*}{\sigma} = 2.0116 - 1.0647\eta + 0.0538\eta^2 \quad \text{......(14)}$$

$$g_m = 1.0286 - 0.6095\eta + 3.5781\eta^2 - 21.3651\eta^3 + 42.6344\eta^4 - 33.8485\eta^5 \quad \text{......(15)}$$

3. COMPUTATIONAL DETAILS

We use FORTRAN programming language for the analysis of radial distribution function at different densities. With the help of PY approximation, we wrote a program in FORTRAN to test the graph of radial distribution function, $g(r) versus \left(\frac{r}{\sigma}\right)$ with different values of densities and sigma.

A listing of a FORTRAN program with the help of above equations gives the exact hard sphere radial distribution function. It inverts the Laplace transform of Percus-Yevick rg(r) that brings g(r) into the agreement with the computer (Monte Carlo and Molecular dynamics) results. With the help of above formulas, we constructed the FORTRAN program and visualize in the graph with the help of xmgrace or gnuplot and analyze the radial distribution function.

4. RESULTS AND DISCUSSION

4.1 Radial Distribution Function of Hard Spheres At Low, Medium and High Densities

In this section, we have presented the main findings of the work. From PY approximation, we wrote a program in FORTRAN to test the graph of radial distribution function, $g(r)$ versus $\left(\frac{r}{\sigma}\right)$ with different values of densities and sigma and obtained the different graphs.

Figure 1 shows the variation of g(r) with distance between the particles at low densities ranging from 0.2 to 0.4. At low densities, the RDF have a single peak at a distance corresponding to the hard sphere diameter, indicating that the particles are well-separated and not interacting with each other. For densities less than 0.2 i.e. $\rho\sigma^3 < 0.2$, the radial distribution function of hard spheres fluid shifts it's shape from oscillatory to monotonic shape. The inconsistency in the shape or profile of g(r) that exceed the experimental errors are noticed with the increment of density.

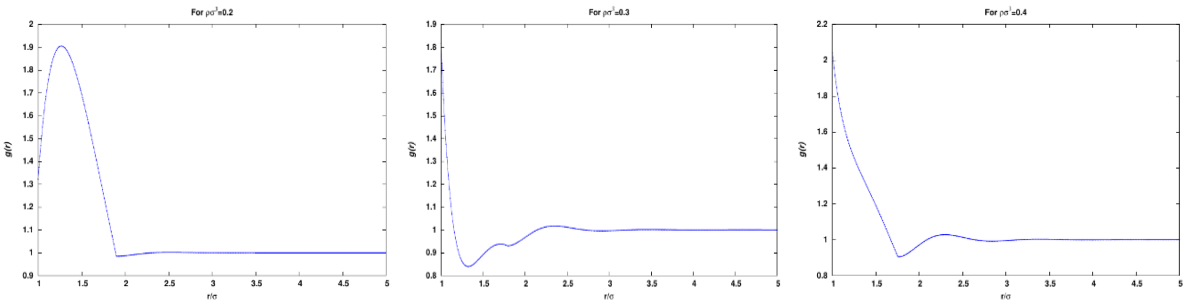

Fig. 1: Graph (a), (b) and (c) shows radial distribution function, g(r) vs the reduced distance $\frac{r}{\sigma}$ for hard spheres at densities 0.2, 0.3 & 0.4 (Low).

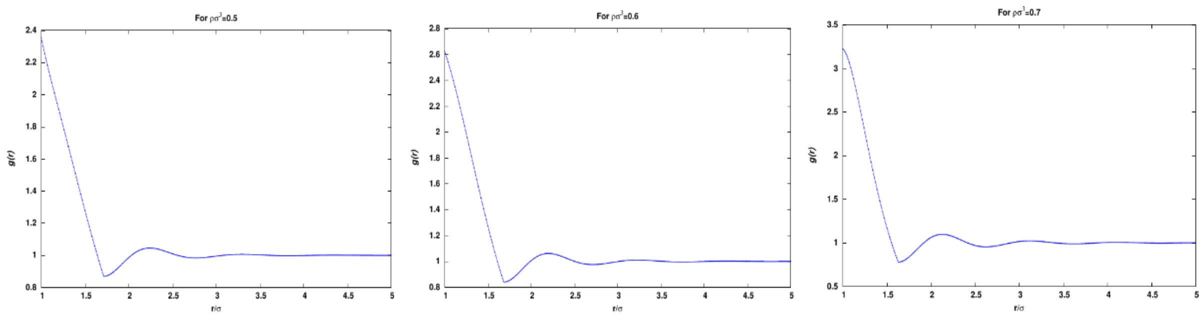

Fig. 2: Graph (a), (b) and (c) shows radial distribution function, g(r) vs the reduced $\frac{r}{\sigma}$ for hard spheres at densities 0.5, 0.6 & 0.7 (Medium).

Figure 2 shows the variation of g(r) with distance between the particles at medium densities ranging from 0.5 to 0.7. As the density increases, the peak becomes broader and shifts to smaller distances, indicating that the particles are coming into closer contact and interacting more strongly with each other. Particularly, in the density area $0.4 < \rho\sigma^3 < 0.6$, the position of the minimal of $g^{PY}(r)$ is orderly move towards lightly larger separations. Nevertheless, when the density increases, for $\rho\sigma^3 > 0.5$ the trend is reversed. The peak at the pioneer position or first peak is the sharpest one indicating the first coordination sphere of the liquid. Then, the preceding peaks will be occurring roughly in the range of gap or intervals of σ but must be smaller than that of pioneer or first peak. Liquids do not have exact intervals as they are more loosely packed than that of solids. The radial distribution function refers to the difference in density of adjacent matter due to distance from a point.

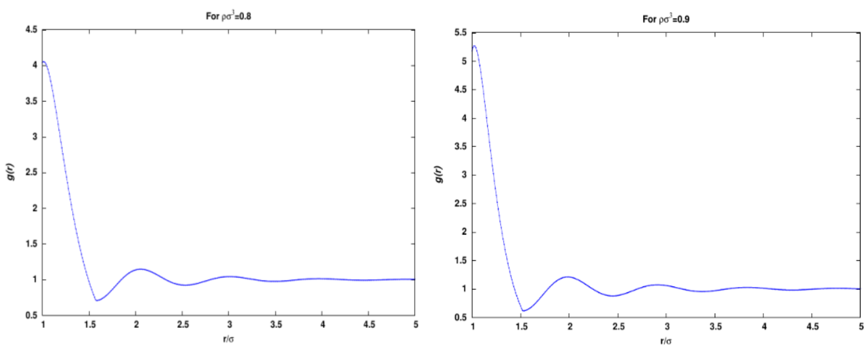

Figure 3: Graph (a) and (b) shows radial distribution function, g(r) vs the reduced distance $\frac{r}{\sigma}$ for hard spheres at densities 0.8 & 0.9 (High).

Figure 3 shows the variation of g(r) with distance between the particles at high densities 0.8 and 0.9. At very high densities, the RDF will become a more complex function with multiple peaks, reflecting the formation of local structures such as crystalline or glassy phases. The hard sphere radial distribution function, g(r) displays a typical shoulder beyond the densities of 0.9 in which roughly random close packing areas begins indicating that there is development of amorphous or crystalline like structure which is not in the principle described by g(r). The hard sphere model of liquid shows the repulsive behavior. When atoms overlap, this liquid has zero density. Liquids cannot maintain a constant structure as it can move in dynamical manner and they lose all long-range structure. It is important to note that the RDF only gives information about the average structure of the system, so a more detailed information about the local structure is obtained by using other techniques such as X-ray diffraction or Molecular dynamics simulations.

5. CONCLUSIONS

In this work, we have studied the RDF of hard spheres at different densities ranging from 0.2 to 0.9 using computational method. From the analysis, we observe that the RDF changes with change in density of the system of hard spheres as expected. At low densities, the RDF have a single peak at a distance corresponding to the hard sphere diameter, indicating that the particles are well-separated and not interacting with each other. As the density increases, the peak becomes broader and shifts to smaller distances, indicating that the particles are coming into closer contact and interacting more strongly with each other. The height of the peaks also increases, indicating that the probability of obtaining a particle at a certain distance from another particle is higher. At very high densities, the RDF becomes a more complex function with multiple peaks, reflecting the formation of local structures such as crystalline or glassy phases.

The estimated radial distribution function, g(r) shows a reliable overall agreement with the data obtained from simulation. The inconsistency in the shape of g(r) that exceed the experimental errors are noticed from the increment of density. The HS radial distribution function, g(r) displays a typical shoulder beyond the densities of 0.9 in which roughly random close packing areas begins indicating the development of amorphous or crystalline like structure.

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