Distribution Functions in Systems of Hard Dumbbells and Linear Hard Triatomics near a Hard Wall

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An extension of the theoretical approach to determine the distribution function in the inhomogeneous systems of hard spheres near a planar hard wall (based on the evaluation of the background correlation function in terms of the residual chemical potentials of the hard particle, hard wall, and the corresponding combined body) is extended to inhomogeneous systems of hard dumbbells (HD) and hard triatomics (HT). The perpendicular and parallel orientations of both HD and HT with respect to the hard wall are considered, and the way of the evaluation of the residual chemical potentials in terms of the geometric quantities—a volume, surface area, and the mean curvature integral, divided by 4π—of a particle, hard wall, and the corresponding combined body is outlined. The inhomogeneous systems hard wall + hard dumbbell with the site−site distance $L^* = 0.6$ and reduced density $\rho^* = 0.491$ and hard wall + hard triatomics with $L^* = 1.6$ and packing fraction $y = 0.409$ are studied, and the obtained distribution functions are compared with simulation data. A fair agreement in the most important range of distances was found.

1. Introduction

For many years there has been a permanent effort to understand the formation of the structure and its characterization in the case of inhomogeneous fluid−solid systems. Both the simulation and theoretical papers (devoted formerly to studies of simple systems composed of monatomic fluids) have focused at present most often on the behavior of molecular fluids. Because the fluid structure depends mainly on the short-range repulsive forces, main traits of the fluid behavior near a hard wall can be elucidated from studies of the hard bodies near a hard wall. A solution of the integro-differential or integral equations[1−6] (e.g., Ornstein−Zernike equation with the closure of the Percus−Yevick type, RISM) or an application of the density functional theory[7−10] (DFT) offers an accurate description of the simple inhomogeneous systems via the hard sphere + hard wall distribution function or the fluid density profile. Within the mentioned methods, some additional approximations and/or input data on the behavior of the corresponding homogeneous system are to be supplied, and the structural characteristics are often obtained by numerical procedures. These facts limit applications of both the methods mainly to inhomogeneous systems of pure homonuclear fluids or to binary mixtures of hard spheres (near a hard wall).

An alternative to the above-mentioned approaches represents a simple method of determining distribution functions via calculation of the background correlation function (bcf) from an expression, which relates bcf to the residual chemical potentials of the considered hard body, hard wall, and the corresponding combined body. The method is grounded on the idea of Meeron and Siegert[11] and further developed by Ballance and Speedy,[12] Smith and Speedy,[13] Labík et al.,[14,15] and others.[16,17]

Recently, the present author slightly modified the approach by introducing the so-called enlarged combined body,[18−21] e.g., enlarged hard dumbbell instead of the dumbbell (resulting from overlapping of a pair of hard spheres). This new type of the combined body has enabled a better description of the homogeneous systems,[18] including the behavior of binary and ternary mixtures,[19] but especially treating the inhomogeneous systems,[20] such as those of hard spheres near a hard wall or in a spherical pore.

In this contribution we aim at extending the method to hard nonspherical bodies near a planar hard wall. Unlike the hard sphere−hard wall system, the distribution function depends also on the orientation of the (nonspherical) body with respect to the hard wall normal; there are two specific orientations of hard dumbbells,[2] considered most often in theoretical and simulation studies: perpendicular and parallel ones. The determination of the structure in the latter case brings new problems; on the other hand, with decreasing the slab thickness (or pore diameter), the description of the structure of the parallel hard bodies gains on its importance.

The paper is organized as follows: In the first part we outline briefly the basic relations and the way of determining the geometric characteristics of hard bodies in the case of pure homogeneous hard sphere systems and in the case of the inhomogeneous hard sphere−hard wall system. The next part deals first with the pure hard dumbbell (HD) systems; expressions for the geometric quantities (the HD volume, surface area, and the mean curvature integral, divided by 4π) for the both studied (parallel and perpendicular) orientations are given. Finally, an extension of these expressions to higher linear objects is discussed. In the following part distribution functions for several inhomogeneous systems are compared with simulation data and results from more involved methods. In conclusion, we discuss the main traits of the used method, its limits, and possible further applications to more complicated systems.

2. Theory

Let us consider a system of N hard spheres (HS) in the volume V with number density $\rho = N/V$. The background (cavity) correlation function of a pair of molecules 1−2 with the center-to-center distance, s, and the reduced distance $x = s/\sigma$ (where σ denotes a diameter) is defined[14] as

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$$Y(x,\rho) = \frac{V^2}{Z_N}\int\cdots\int\prod_{i\geq 2} e_{1i}\prod_{j\geq 2} e_{2j}\prod_{j>i>2} e_{ij}\,d(3)\cdots d(N) = e^{\beta u_{ij}(x)} g_{ij}(x,\rho)$$

Here u_{ij} denotes the interaction pair potential, $\beta = 1/k_B T$, where k_B is the Boltzmann constant and T the temperature, Z_N is the configuration integral (of N molecules), and $e_{ij} = \exp[-\beta u_{ij}]$. It is evident that for distances larger than x_c (where x_c stands for the contact distance, in the case of HS $x_c = 1$) $g_{ij} = Y_{ij}$.

The manyfold integral in the last equation can be interpreted[14] as the configurational integral of one hard diatomic (HD) and $(N - 2)$ hard spheres, $Z_{N-2,1}$. By subtracting and adding the same term $Z_{N-2,0}$, one obtains

$$\ln Y = [\ln Z_{N-2,1} - \ln Z_{N-2,0}] - [\ln Z_{N,0} - \ln Z_{N-2,0}] = -\beta\Delta\mu^{HD} + 2\beta\Delta\mu^{HS}$$

where $\Delta\mu^{HD}$ and $\Delta\mu^{HS}$ stand for the residual chemical potential (i.e., difference of the function of a fluid and perfect gas) of a diatomic (1−2) and that of hard spheres. A similar conclusion can be drawn for other hard body systems as well. Omitting indices (HS) of the chemical potentials of the studied pair of molecules and writing for the combined body (the generalization of a diatomic, originating by overlapping of two hard spheres), μ^{CB}, instead of μ^{HD}, we can write the basic relation

$$\ln Y_{ij}(r,\rho^*) = \Delta\mu_i/kT + \Delta\mu_j/kT - \Delta\mu^{CB}(r)/kT \quad (1)$$

The expression for the residual chemical potential follows from the residual Helmholtz energy of individual molecules and that of the (infinitely diluted) combined body. In our previous study[22] of the self-consistent equation of state and the chemical potential, we have proposed an expression for the residual Helmholtz function, ΔA, of the general hard (convex) body system in a form

$$\frac{\Delta A}{Nk_BT} = -\ln(1-y) + \frac{3\alpha y}{1-y} + \frac{\beta y^2(3/2 - y/3)}{(1-y)^2}$$

where y is the packing fraction and α, β are two nonsphericity parameters: $\alpha = RS/3V$ and $\beta = QS^2/9V^2$. R, S, V, and Q stand for the geometric characteristics of the considered bodies: the mean radius (exactly the mean curvature integral, divided by 4π), surface area, and volume; for functional Q, of the dimension $[l^2]$, it holds true $R^2 \geq Q \geq S/4\pi$.

For the pure hard sphere system, where $\alpha = \beta = 1$, the compressibility factor, PV/Nk_BT, corresponding to eq 1 at the packing fraction $y = 0.5$ exceeds the generally accepted value (cf. 13.166 vs 13.00). Therefore, we slightly modified the y^3 coefficient of the last equation; i.e., we used 5/12 instead of 1/3 (resulting in $PV/Nk_BT = 12.96$). The general expression for Helmholtz energy of a solution, ΔA_s, reads then as

$$\frac{\Delta A_s}{Nk_BT} = -\ln(1-y) + \frac{3\alpha_s y}{1-y} + \frac{\beta_s y^2(3/2 - 5y/12)}{(1-y)^2} \quad (2)$$

The residual chemical potential of the pure fluid is

$$\Delta\mu/kT = -\ln(1-y) + \left[\frac{y}{1-y}\right][6\alpha + 1] + \left[\frac{y}{1-y}\right]^2\left[3\beta\left(\frac{3}{2} - \frac{y}{3}\right) + 3\alpha\right] + \frac{\beta}{3}\left[\frac{y}{1-y}\right]^3(7 - y/2) \quad (3)$$

[For hard spheres at $y = 0.5$ one finds $\Delta\mu/kT = 16.94$ in comparison with 17.19 from the previously considered expression.]

For the residual chemical potential of the infinitely diluted combined body in the considered hard bodies (b) holds similarly

$$\Delta\mu^{CB}/kT = -\ln(1-y) + \left[\frac{y}{1-y}\right][(3\alpha(R^* + S^*) + V^*] + \left[\frac{y}{1-y}\right]^2\left[\beta(Q^* + 2S^*)\left(\frac{3}{2} - \frac{y}{3}\right) + 3\alpha V^*\right] + \frac{1}{3}\left[\frac{y}{1-y}\right]^3(7 - y/2)\beta V^* \quad (4)$$

where an asterisk denotes the reduced quantities ($R^* = R^{CB}/R_b$, $S^* = S^{CB}/S_b$, $Q^* = Q^{CB}/Q_b$, $V^* = V^{CB}/V_b$). If we define further $\Delta r = R_i^* + R_j^* - R^{*CB}$, $\Delta s = S_i^* + S_j^* - S^{*CB}$, $\Delta v = V_i^* + V_j^* - V^{*CB}$, and $\Delta q = Q_i^* + Q_j^* - Q^{*CB}$, then

$$\ln Y_{ij} = -\ln(1-y) + \left[\frac{y}{1-y}\right][(3\alpha(\Delta r + \Delta s) + \Delta v] + \left[\frac{y}{1-y}\right]^2\left[\beta(\Delta q + 2\Delta s)\left(\frac{3}{2} - \frac{y}{3}\right) + 3\alpha\Delta v\right] + \frac{\beta}{3}\left[\frac{y}{1-y}\right]^3(7 - y/2)\Delta v \quad (5)$$

2.1. System of Hard Spheres. ***Homogeneous System.*** In the case of pure (homogeneous) hard sphere (HS) systems, all the reduced geometric quantities are equal to one; i.e. $R^* = S^* = V^* = Q^* = 1$. For the combined hard body, corresponding to the given hard spheres, we considered previously[16] a hard dumbbell (HD), resulting from overlapping of a pair of HSs with the HS distance $x = s/\sigma$ where s denotes the HS center−center distance. In the present version[18] we have used instead of the HD an enlarged hard dumbbell (EHD). The enlarged hard dumbbells are also used as models of diatomics (discussed later on).

Employing the method of Connolly,[23,24] one can write for distances $x \leq \sqrt{3}$ the following expression for the surface area, S, of the homonuclear CB

$$S = 2[2\pi r^2(1 + \sin\theta) + 2\pi r_p{}^2(2\theta\cos\theta - \sin\theta)] \quad (6)$$

or

$$S^* = 1 + 2\theta\cos\theta \quad (7)$$

where $\theta = \arcsin(x^*/2)$. In eq 6 the former term corresponds to the convex part, denoted in Figure 1, by symbol A (this term, S_c, is given by an arc, depending on the radius r and angle $\pi/2 + \theta$); the latter term (S_{sad}) corresponds to the saddle part, C [with the probe radius $r_p = r = \sigma/2$, $S_{sad}/2 = 2\pi r_p\int_0^\theta X\,d\theta'$ where $X = D - r_p\cos\theta'$ and $D = 2r\cos\theta$]. The conical part, B, does not contribute to S, however, by $V_{con}/2 = \pi r^3\cos^2\theta\sin\theta/3$ to volume V.

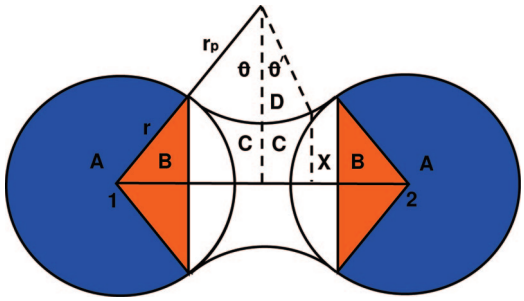

Figure 1. Geometry of the enlarged hard diatomics (for the center−center distance $d > \sigma$). A = the convex part (blue), B = conical part (orange), and C = saddle part (white) with radius $r_p = r$, $r = \sigma/2$ = hard sphere radius. 1, 2 = hard sphere origins, D = torus radius.

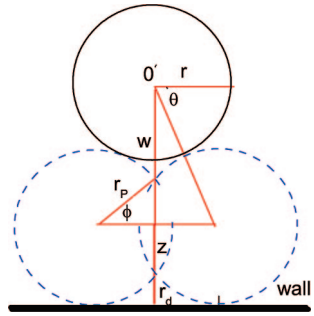

Figure 2. Geometry of the hard sphere near a hard wall (represented by the thick line); z = the hard sphere distance from the wall, $w = (z - 0.5)/\sigma$; dashed circles = the probe hard spheres with radius $r_p = r$; r_d = radius of the disk.

The reduced EHD volume is then given by a sum of contributions of the convex, cone, and saddle parts [$V_c = S_c r/3$, $V_{sad}/2 = \pi r_p \int_0^\theta X^2 \cos\theta' \, d\theta'$]

$$V^* = 1 + 2\sin\theta + 4\cos^2\theta\sin\theta - 3\theta\cos\theta \qquad (8)$$

Connolly did not consider the evaluation of the mean radius, R. Here we employ the relation, valid for majority of convex bodies (with exception of a cube, tetrahedron, etc.)

$$R_c = \partial S_c/\partial r$$

For the saddle part of R

$$R_{sad} = -\partial S_{sad}/\partial r_p$$

Then

$$R^* = 2R/\sigma = 1 + 2\sin\theta - \theta\cos\theta \qquad (9)$$

When the geometric functionals for CB and HS are substituted in eq 2, a fair agreement of the radial distribution functions with simulation data is obtained in the whole range of densities, as shown in our previous paper.[20]

Hard Spheres near a Hard Wall. Extensions of the PY or DFT approaches to determine the hard sphere structure near a hard wall are grounded on the idea that such heterogeneous systems are just a special−limiting−case of the HS mixtures, where the concentration of one component with infinitely large diameter tends to zero.

In the present approach we consider in eq 1 a pair of different hard bodies: a hard sphere and an infinitely thin disk (a part of the infinitely large HS); see Figure 2. The disk possesses only one circular surface area, with its normal oriented toward the interacting hard sphere a distance z apart; the disk diameter equals to the distance between contact points of two probe hard spheres. Its mean radius $R_d = 0$.

The contribution of the convex part of the CB to surface area, S, and similarly to R and V is just a half of the value for a pair of two HSs. In the case of saddle parts we have to consider in the respective integrals the angle interval $(-\pi/2, \theta)$, where now $\arcsin\theta = w$ and $w = (z - 0.5)/\sigma$. The geometric quantities of the CB are

$$R^{*CB} = 1 + \sin\theta - \frac{1}{2}\left(\frac{\pi}{2} + \theta\right)\cos\theta \qquad (10)$$

$$S^{*CB} = \left(\frac{\pi}{2} + \theta\right)\cos\theta \qquad (11)$$

and

$$V^{*CB} = 1 + \sin\theta - \frac{3}{2}\left(\frac{\pi}{2} + \theta\right)\cos\theta + \cos^2\theta(2\sin\theta + 3) \qquad (12)$$

whereas the corresponding characteristics of the disk are $R_j^* = V_j^* = 0$ and $S_j^* = \cos^2\theta$.

The quantity Q^{*CB} of the combined body is approximated as

$$Q^{*CB} = S^{*CB}[(R^{*CB})^2/S^{*CB}]^{1/4} \qquad (13)$$

and for Q_j^* of the disk we assume $Q_j^* = S_j^*(\pi^2/8)^{1/4}$.

In the interval of $w \in (\sqrt{3}/2, 1)$ the combined body decomposes into two pieces (with cusps); their shapes depend on angle ϕ (see Figure 2). As a result, one has to subtract δR^*, δS^*, and δV^* from the contributions of the saddle part of the single geometric quantities. Thus

$$\delta R^* = \sin\phi - \phi\cos\theta \qquad (14)$$

$$\delta S^* = -\sin\phi + 2\phi\cos\theta \qquad (15)$$

$$\delta V^* = \sin\phi - 3\phi\cos\theta + 2\cos^2\theta\sin\phi \qquad (16)$$

In Figure 3, a comparison is given of the theoretical distribution function wall–sphere (WS), g_{WS}, with simulation data.[2] Fair agreement is found in the most important region of z, $z/\sigma \in (0.5, 1.5)$.

3. Hard Diatomics

3.1. Pure Hard Dumbbells. Before we describe the inhomogeneous system of hard dumbbells near a hard wall, we will consider a simpler homogeneous systems of (pure) hard dumbbells. There are two limiting orientations of a pair of HDs, i.e. end-to-end and parallel ones. In the former case the (linear) combined body is composed of four hard spheres, two and two with the reduced site−site (s−s) distances, $L^* = l/\sigma$, and one with center−center (c−c) distance s ($= x\sigma$). These distances determine three saddle parts of the combined body. The distribution function varies only with the reduced distance $x = s/\sigma$. Thus, it is possible to express the geometric quantities of CB as a sum of values for two individual EHDs (with a lessened convex parts of the interacting sites) plus the central saddle contribution. We can write

$$R^{*CB} = 2R_i^* - 1 + 2\sin\theta - \theta\cos\theta \quad (17)$$

$$S^{*CB} = 2S_i^* - 1 + 2\theta\cos\theta \quad (18)$$

$$V^{*CB} = 2V_i^* - 1 + 2\sin\theta + 4\cos^2\theta\sin\theta - 3\theta\cos\theta \quad (19)$$

where

$$R_i^* = 1 + L^* - \chi\cos\chi, \quad S_i^* = 1 + 2\chi\cos\chi \quad (20)$$

$$V_i^* = 1 + L^* - L^{*3}/2 - 3\chi\cos\chi \quad (21)$$

(with $\arcsin\chi = L^*/2$).

Determination of the geometric quantities of a pair of parallel hard dumbbells is slightly more complicated: It is useful to consider separately the hemispheres of both the HDs (altogether characterized by eqs 6−9) and the roughly cylindrical part. In the simpler approach one can take this part as a combination of two cylinders of the reduced length L^* a distance x apart with distance w greater than $\sqrt{3}/2$. The contributions of the cylindrical part to the CB are then

$$\Delta_{cyl}R^* = L^*/2, \quad \Delta S_{cyl}^* = L^*(1 + 4\theta/\pi) \quad (22)$$

$$\Delta V_{cyl}^* = (12/\pi)L^*(\cos\theta\sin\theta + \pi/8) \quad (23)$$

In the more correct approach we take into consideration the saddle part of the original dumbbells and request that $X_{saddle}^* = X_{i,saddle}^*$ for $x = 0$. Then

$$\Delta_{cyl}R^* = L^* - \chi\cos\chi, \quad \Delta S_{cyl}^* = 2\chi\cos\chi(1 + 4\theta/\pi) \quad (24)$$

$$\Delta V_{cyl}^* = (8/\pi)(3L^* - L^{*3}/2 - 3\chi\cos\chi) \times (\cos\theta\sin\theta + \pi/8) \quad (25)$$

where $\chi = \arcsin(L^*/2)$ as mentioned before. When $\Delta_{cyl}R^*$, ΔS_{cyl}^*, and ΔV_{cyl}^* are added to (6)−(9) and the differences in the respective geometric functionals substituted in eq 2, fair results for the background correlation function, Y, are obtained (cf. ref 14), as indicated in Figure 4. It is thus plausible to extend the latter approach to inhomogeneous systems.

3.2. Hard Dumbells near a Hard Wall. ***Perpendicular Orientation.*** Similarly as in the case of inhomogeneous system of hard spheres we consider the small piece of the hard wall to be a special hard convex body: an infinitely thin disk with only one side surface area and with the mean radius and volume equal to zero. From similar approach like before we obtained for the combined body of the hard dumbbell−hard wall system

$$R^{*CB} = R_i^* + \sin\theta - \frac{1}{2}\left(\frac{\pi}{2} + \theta\right)\cos\theta \quad (26)$$

$$S^{*CB} = S_i^* - 1 + \left(\frac{\pi}{2} + \theta\right)\cos\theta \quad (27)$$

and

$$V^{*CB} = V_i^* + \sin\theta - \frac{3}{2}\left(\frac{\pi}{2} + \theta\right)\cos\theta + \cos^2\theta(2\sin\theta + 3) \quad (28)$$

where R_i^*, S_i^*, and V_i^* are defined above.

Geometric Quantities for Distances Greater Than $\sqrt{3}$. If the distance of the site and wall, w, is larger than $\sqrt{3}$, then the combined body decomposes into two parts (see Figure 2). In both the case of a pair of diatomics and that of diatomic near

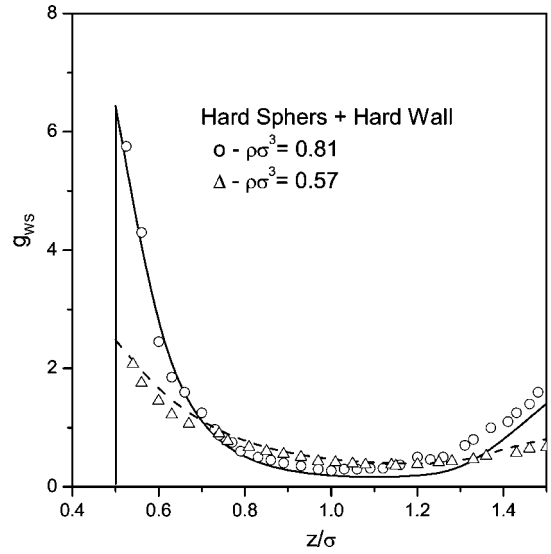

Figure 3. Distribution functions in the systems of hard spheres near a hard wall. z/σ = the reduced hard sphere distance from the wall; ○, △ = simulation data taken from figures of ref 2; full and dashed lines = theoretical functions.

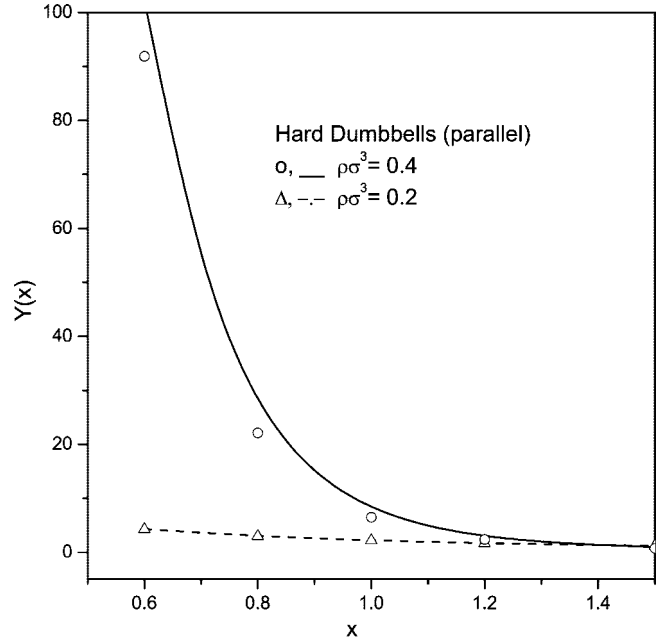

Figure 4. Background correlation function of parallel hard dumbbells. x = the reduced site−site distance; ○, △ = simulation data from ref 14.

a hard wall, it is necessary to subtract from the formulas for the saddle parts small quantities δR^*, δS^*, and δV^* given by eqs 14−16.

Parallel Orientation. The problem of determining geometric quantities in the case of a dumbbell parallel to a hard wall can be solved by considering separately outer hemispheres of DB as one hard sphere in addition of the roughly cylindrical part, both near a hard wall. Following the method proposed for homogeneous parallel DBs we can write

$$R^{*CB} = (R_i^* + 1)/2 + \sin\theta - \frac{1}{2}\left(\frac{\pi}{2} + \theta\right)\cos\theta + \frac{1}{2}(2\sin\chi - \chi\cos\chi) \quad (29)$$

$$S^{*CB} = (S_i^* - 1)/2 + \left(\frac{\pi}{2} + \theta\right)\cos\theta + \chi\cos\chi(1 + 4\theta/\pi) \quad (30)$$

and

$$V^{*CB} = (V_i^* + 1)/2 + \sin\theta - \frac{3}{2}\left(\frac{\pi}{2} + \theta\right)\cos\theta + \cos^2\theta(2\sin\theta + 3) + (9/4\pi)(6\sin\chi - \sin^3\chi/2 - 3\chi\cos\chi)\left(2\cos\theta(1 + \sin\theta) - \frac{\pi}{4}\right) \quad (31)$$

For larger HD−wall separations, $w \geq \sqrt{3}/2$, one has to subtract corrections (functions of ϕ) similar to those given for the system HS + hard wall. In the case of parallel orientation we consider instead of the hard disk a two-dimensional infinitely thin dumbbell with HS diameter equal to $\cos^2\theta$.

4. Hard Triatomics near a Hard Wall

Expressions for the geometric functionals, used for the determination of the distribution functions for either the perpendicular or parallel orientations of the (linear) triatomics with respect to the hard wall, are just simple extensions of the relations derived for hard dumbbells. If the considered model consists of n overlapping hard spheres of the same diameters and s−s distances, then the geometric quantities can be expressed in terms of those of hard dumbbell, i.e.

$$R^{*m} = 1 + m(R^{*HD} - 1), \quad S^{*m} = 1 + m(S^{*HD} - 1), \quad V^{*m} = 1 + m(V^{*HD} - 1) \quad (32)$$

where generally $m = n - 1$; in case of triatomics (t), $m = 2$. For the perpendicular orientation one can use eqs 26−28 after substitution of R^{*t}, S^{*t}, V^{*t} for R_i^*, S_i^*, V_i^*.

In the case of the parallel orientation the following expressions hold true

$$R^{*CB} = (R_i^{*m} + 1)/2 + \sin\theta - \frac{1}{2}\left(\frac{\pi}{2} + \theta\right)\cos\theta + \frac{m}{2}(2\sin\chi - \chi\cos\chi) \quad (33)$$

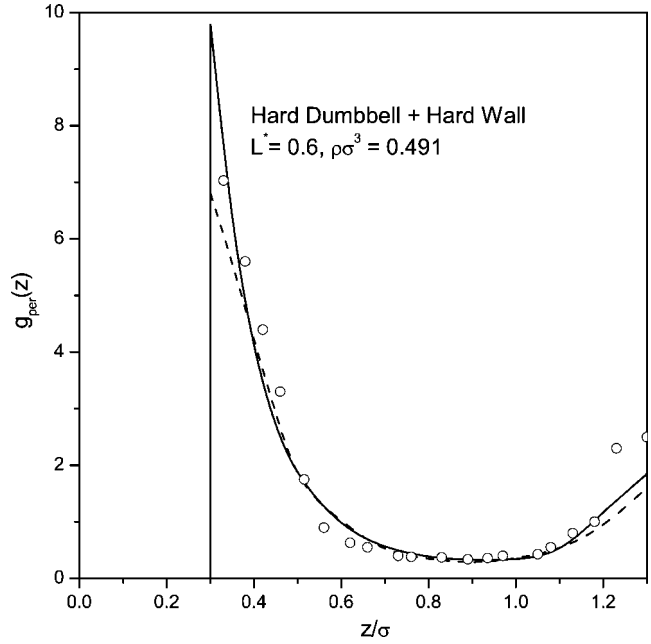

Figure 5. Distribution function of the perpendicular hard dumbbell ($L^* = 0.6$, $y = 0.491$) near the hard wall. z/σ = the reduced hard sphere distance from a wall. ○ = simulation data taken from figures in ref 8.

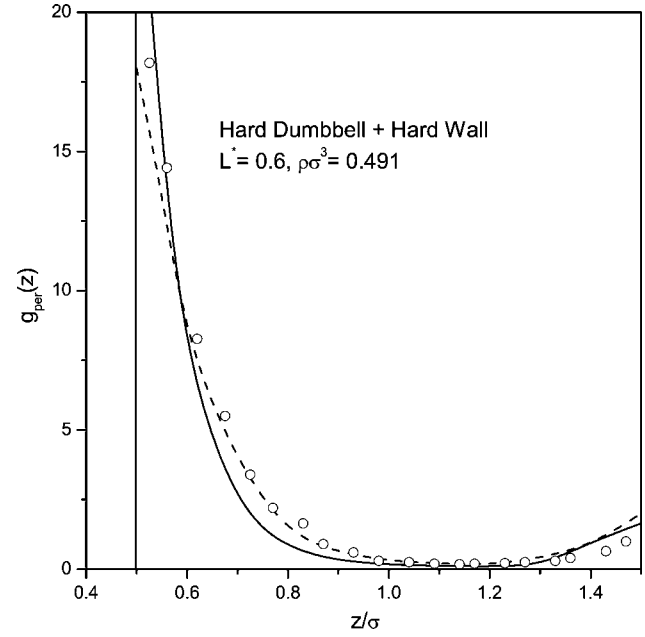

Figure 6. Same as in Figure 4 but for parallel orientation.

$$S^{*CB} = (S_i^{*m} - 1)/2 + \left(\frac{\pi}{2} + \theta\right)\cos\theta + m\chi\cos\chi(1 + 4\theta/\pi) \quad (34)$$

and

$$V^{*CB} = (V_i^{*m} + 1)/2 + \sin\theta - \frac{3}{2}\left(\frac{\pi}{2} + \theta\right)\cos\theta + 2\cos^2\theta(\sin\theta + \frac{3}{2}) + (9m/4\pi)(6\sin\chi - \sin^3\chi/2 - 3\chi\cos\chi)\left(2\cos\theta(1 + \sin\theta) - \frac{\pi}{4}\right) \quad (35)$$

where again $m = 2$.

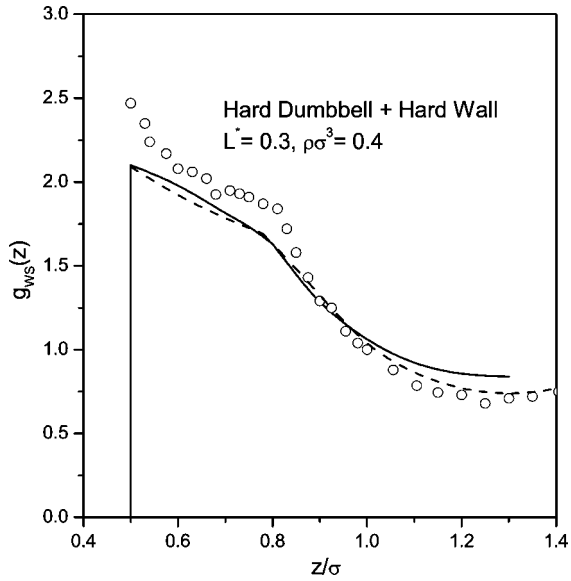

Figure 7. Full site−wall distribution function of hard dumbbells ($L^* = 0.3$, $\rho^* = 0.4$): (○) simulation data, (---) results of RISM approach, both taken from figures of ref 2.

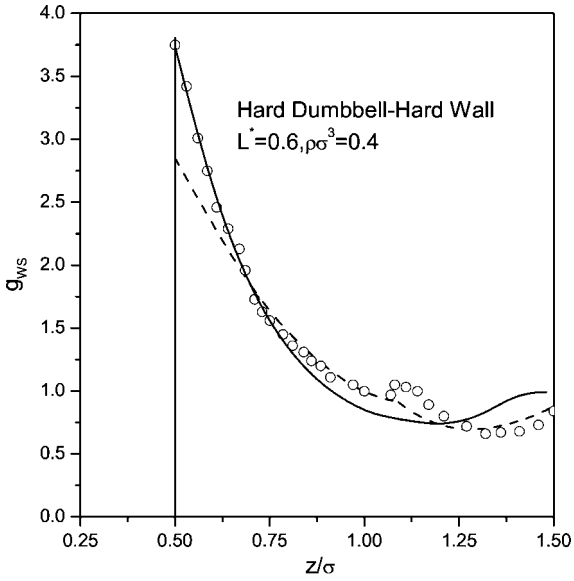

Figure 8. Same as in Figure 7 but for $L^* = 0.6$.

5. Results and Discussion

The site−wall distribution function in the inhomogeneous systems of hard dumbbells near the planar hard wall were studied experimentally (Monte Carlo simulations) by Henderson et al.[8] for dumbbells of $L^* = 0.2$, 0.4, and 0.6 at different reduced densities. In Figures 5 and 6 we compare our results determined for the hard dumbbell of $L^* = 0.6$ and the reduced density $\rho^* = 0.491$ with the pseudo-experimental data and values of $g(z)$ obtained by solution of the integral equation with the PY closure (referred[8] for both the perpendicular and parallel orientations). It is apparent that our results agree well (better than PY ones) with the pseudo-experimental data in the region of small distances, less well for $w > \sqrt{3}/2$.

In principle, from the values of the distribution functions for the limiting orientations one can determine the full site−wall distribution function. Here we consider the simplest approximation; i.e., we take only g_{per} and multiply it by ratio of the possible orientations of HD vs wall to all the orientations (for angle π). Distribution function g_{WS} of (wall + site) system from this

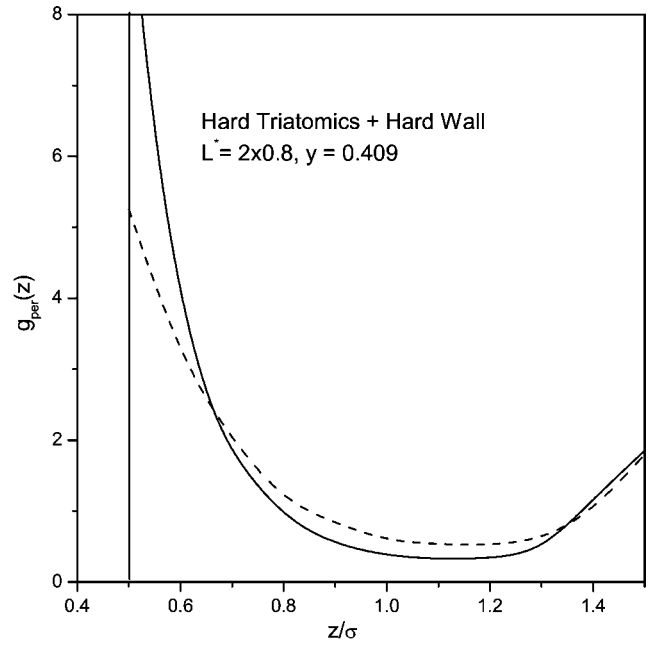

Figure 9. Distribution function of the perpendicular hard triatomics (outer site $L^* = 1.6$, $y = 0.409$): (—) theoretical; (---) simulation results taken from figures of ref 21.

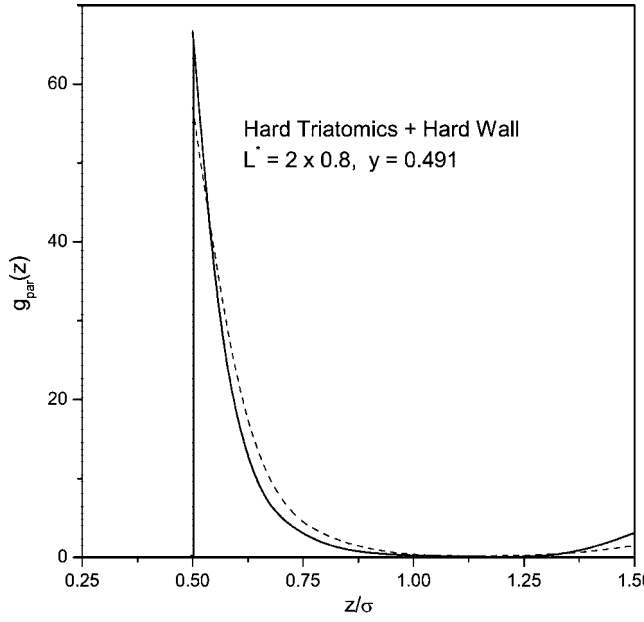

Figure 10. Same as in Figure 9 but for parallel orientation.

simple approximation is shown in Figures 7 and 8 for systems with $\rho^* = 0.4$ and $L^* = 0.3$ and 0.6, respectively; pseudo-experimental values and results from the PY-like approach (taken from graphs in ref 3) are plotted for comparison. Close to the contact distance both the methods (PY and present ones) yield similar results; PY works better for distances $w \approx L^*/2$. An inclusion of the values of g_{par} into the evaluation of g_{WS} will probably improve an agreement of the theory with experiment for short site−wall distances; an effect of the combination of g_{per} and g_{par} on g_{WS} elsewhere is hard to judge.

Simulation results for the perpendicular and parallel orientations of triatomics of $L^* = 1.6$ ($L^* = 2 \times 0.8$), $y = 0.409$ were referred by Nezbeda et al.[21] A comparison of the g_{per} and g_{par} dependence on z/σ with the simulation results (smooth curves in figures of ref 21) is given in Figures 9 and 10. Quite surprisingly, larger deviations are found in the case of the

perpendicular orientation, whereas a fair agreement of the calculated and experimental distribution functions for the parallel orientation, g_{par}, is unexpected.

6. Conclusion

In this paper we extended the "geometric" method of determining correlation functions to inhomogeneous systems, composed of nonspherical hard particles near a hard wall. Because the systems studied are related to the behavior of HSs in the colloidal limit, we slightly modified the equation for the residual chemical potential. It was shown that introduction of the nonspherical hard bodies (i.e., diatomics, linear triatomics, etc.) requires a solution of specific geometric problems for the saddle parts. We formulated two approximations which seem to work quite well. More exact evaluation of the surface area and volume of the combined body (applying Connolly's method) respects the limiting condition $X^{*WS} = X_i^*$ for $x = 0$ in the case of pure dumbbell; some uncertainty arises with the determination of the corresponding mean curvature integrals.

The main trait of the "geometric" method is its great simplicity and applicability to large variety of problems. The accuracy of the prediction of the structure characteristics of simple systems is quite fair. In the case of inhomogeneous systems of hard diatomics or triatomics, it is difficult to estimate the accuracy (of theoretical distribution functions) as the pseudo-experimental data are presented only in the form of small figures, from which only part is used for comparison.

The method can be extended to characterize the structure of mixtures of different hard bodies, similarly as in the case of hard spheres. In summary, the "geometric method" offers a simple tool to determine the structure of various inhomogeneous systems in the most important region.

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