DISTRIBUTION FUNCTIONS OF THE HARD HETERONUCLEAR DUMBBELLS AND OF THEIR MIXTURES WITH HARD SPHERES NEAR A HARD WALL

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Dedicated to Professor Ivo Nezbeda on the occasion of his 65th birthday.

The recently proposed method to determine the hard body distribution function on the basis of values of the residual chemical potentials of a pair of hard molecules and that of the corresponding combined body is applied to describe behavior of the inhomogeneous systems of pure heteronuclear hard dumbbells or a mixture of heteronuclear dumbbells with hard spheres near a hard wall. Two variants of the main orientation of the dumbbells – i.e. the perpendicular orientation with respect to the hard planar wall – are studied and several values of the packing fraction are considered. The used simple method yields a fair prediction of the slices of the distribution function or average correlation function for the heteronuclear dumbbell (composed of two hard spheres with rather different diameters (σ_2/σ_1 = 0.5) and site–site separation (l/σ_1 = 0.625)) near a wall; in the case of mixtures of hard spheres and hard heteronuclear dumbbells the hard sphere diameter $\sigma_{hs} = \sigma_1$.
Keywords: Statistical geometry; Residual chemical potential; Inhomogeneous system; Hard body; Heteronuclear dumbbell; Enlarged hard dumbbell; Hard sphere–hard dumbbell mixture; Thermodynamics; Local density approximation; Density functional theory.

Description of the structure of inhomogeneous hard body (HB) systems plays an important role in understanding adsorption, catalysis, behavior of fluids in nanotubes or behavior of biochemical systems. A fair amount of simulation results for different types of inhomogeneous systems formed by hard spheres (HSs) or non-spherical hard bodies near a hard planar wall, in a slot or in a spherical pore can be found in the literature. Theoretical studies employ mainly the solution of the Ornstein–Zernike integral equation[1,2] or density functional theory (DFT), cf. refs[3–5] and references given therein. Both the approaches have proved to predict fairly well the distance depend-

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ence of the radial distribution function or HB density profile in both the homogeneous and inhomogeneous systems, DFT being at present more often applied. However, evaluation of distribution functions within these methods is not simple and some input data, determined from the equation of state for the bulk phase, are necessary.

Recently we followed in series of papers[6–10] an alternative approach which makes it possible to determine the background correlation function, Y, $Y(x) = \exp[u(x)/kT]g(x)$ (where u and g denote the intermolecular pair potential and radial distribution function, respectively, x is distance and T is temperature) in terms of the residual chemical potentials, $\Delta\mu$, of a pair (triplet ...) of the considered HBs and that of the combined HB originated from overlapping of the considered two (three etc.) particles. The residual chemical potentials of HBs are given in terms of the geometric quantities (functionals) such as the HB volume, surface area, mean radius (mean curvature integral divided by 4π) and others. Thus, this alternative method has a pronouncedly geometric trait; due to this character the method is very simple and straightforward. However, one serious problem occurs with application of this method, namely determination of the geometric functionals of the non-convex combined HB (e.g those of a hard dumbbell in the case of HSs systems, etc.).

In ref.[6] we studied behavior of systems of HSs; the geometric functionals of the combined body, i.e. hard dumbbell were determined as those of the spherocylinder (SC) enveloping the given dumbbell. This approximation appeared to yield precise prediction of the background correlation function (cavity correlation function) for the reduced center-to-center distances $x \in (0,1.5)$, i.e. the direct correlation function in the whole region and part of the distribution function close to the contact distance. However, for distances of approximately $x = 2$ the nonphysical values were found. Another problem encountered in the case of mixtures of spheres differing considerably in their diameters. To improve the determination of the geometric quantities of the combined bodies in such cases we introduced in refs[7–10] a model of the "enlarged hard body" (e.g. enlarged hard dumbbell).

In this paper we apply our method to determine distribution/average correlation function of the heteronuclear hard dumbbell (HHD) in the inhomogeneous HHD–hard wall system. We tackle the problem of application of the method to this system in ref.[10] where a oversimplified geometric view was used. Here we try to improve our consideration/approximation.

In this work we firstly present the general basis of the method and subsequently we derive expressions for the necessary geometric quantities of the HHD and combined bodies. Finally we evaluate the slices through the distribution functions and average correlation functions of the pure HHD + hard wall and mixture (HS + HHD) near hard wall.

THEORY

The starting point of the method is the relation (cf. ref.[11]) between the background (cavity) correlation function, Y, and the residual chemical potentials, $\Delta\mu$, of the pair of considered molecules – hard body (HB) – and the combined hard body (CB) (given by an overlap of the HBs),

$$\ln Y_{ij} = \Delta\mu_i^{\mathrm{HB}} / kT + \Delta\mu_j^{\mathrm{HB}} / kT - \Delta\mu^{\mathrm{CB}} / kT \tag{1}$$

where k and T denote Boltzmann constant and temperature, respectively.

As the inhomogeneous systems of HB near a hard wall are related to the behavior of HB mixtures in the colloidal limit, we started from the self-consistent expression[12] for ΔA_s, where A_s stands for the Helmholtz energy of a solution, such as

$$\Delta A_s / NkT = -\ln(1-v) + 3\alpha_s v/(1-v) + [\beta_s v^2 (3/2 - 5v/12)]/(1-v)^2 . \tag{2}$$

Here v stands for the packing fraction $v = \rho\sum x_j V_j$ of the HB mixture and $\alpha_s = rs/3\rho v$, $\beta_s = qs^2/9\rho v^2$ are two non-sphericity parameters defined in terms of the geometric quantities – the HB volume, V, surface area, S, and the mean curvature integral, divided by 4π, R; for the mixture it holds $r = \rho\sum x_j R_j$, $s = \rho\sum x_j S_j$, $q = \rho\sum x_j Q_j$, where ρ is the number density and x_j the mole fraction. The equation of state corresponding to (*2*) reads as

$$PV_s / NkT = 1/(1-v) + 3\alpha_s v/(1-v)^2 + \beta_s v^2 (3 - 5v/4 + 5v^2/12)/(1-v)^2 . \tag{3}$$

The compressibility factor of pure HSs from this equation at the packing fraction $\eta = 0.5$ equals 12.958 in comparison with MC value 13; Eq. (*3*) yields also a fair description of systems of hard dumbbells and other fused HS bodies.

From Eq. (*2*), one can find the following relation for the residual chemical potential

$$\begin{aligned}\Delta\mu_i / kT = {} & -\ln(1-v) + (sR_i + rS_i + \rho V_i)/(1-v) + \\ & + [(s^2 Q_i + 2qsS_i)(3/2 - v/3) + rsV_i]/[9(1-v)^2] + \\ & + qs^2 (7 - v/2)V_i / [27(1-v)^3] .\end{aligned} \tag{4}$$

Next, we introduce the reduced quantities $V_i^* = V_i/\Sigma x_j V_j$, $S_i^* = S_i/\Sigma x_j S_j$, $R_i^* = R_i/\Sigma x_j R_j$ and $Q_i^* = Q_i/\Sigma x_j Q_j$. Then the above equation can be rearranged to the form

$$\Delta\mu_i / kT = -\ln(1-\nu) + [\nu/(1-\nu)][3\alpha_s(R_i^* + S_i^*) + V_i^*] + [\nu/(1-\nu)]^2 \times$$
$$\times [\beta_s(Q_i^* + 2S_i^*)(3/2 - \nu/3) + 3\alpha_s V_i^*] + [\nu/(1-\nu)]^3(7/3 - \nu/6)\beta_s V_i^*. \quad (5)$$

If we define differences of the reduced geometric quantities as

$$\Delta X^* = X_i^* + X_j^* - X^{\mathrm{CHB}*} = (X_i + X_j - \mathrm{X}^{\mathrm{CHB}})/\Sigma x_j X_j$$

the background correlation function reads as

$$\ln Y = -\ln(1-\nu) + [\nu/(1-\nu)][3\alpha_s(\Delta R^* + \Delta S^*) + \Delta V^*] + [\nu/(1-\nu)]^2 \times$$
$$\times [\beta_s(\Delta Q^* + 2\Delta S^*)(3/2 - \nu/3) + 3\alpha_s \Delta V^*] + [\nu/(1-\nu)]^3(7/3 - \nu/6)\beta_s V^*. \quad (6)$$

From the last equation it is obvious that knowledge of the differences in volumes and other geometric quantities of the pair of HBs and of the combined body are sufficient to determine *Y* and consequently the pair correlation or distribution functions (*c* or *g*).

Geometric Properties of the Enlarged Heteronuclear Dumbbell

Geometric properties of a hard sphere – its volume, *V*, surface area, *S*, and the mean curvature integral divided by 4π, *R*, are simple functionals of radius, r_s, i.e. $V_s = 4\pi r_s^3/3$, $S_s = 4\pi r_s^2$ and $R_s = r_s$. The reduced quantities read as $R_s^* = R_s^*/(\sigma_s/2)$, etc. With the choice $\sigma_s = \sigma_A = \sigma = 2r_1$ all the reduced geometric quantities of HS are equal to one.

For the dumbbell (and other fused HS models), we introduce enlarged hard dumbbell (EHD) – a body "perceived" by the other molecules of the studied system; EHD originates when a probe of the radius r_p is rolled over a hard dumbbell. In the case of homonuclear dumbbell (HD) $\sigma_1 \equiv \sigma_2 = \sigma$ and $r_p = r_1$. If the difference of r_1 and r_2 in the heteronuclear hard dumbbell is small, then we can take $r_p = (r_1 + r_2)/2$; however, in our case we have to use a weighted average, an analogue of the prescription applied in the case of the HS mixtures[10]

$$r_p = \sum_1^2 r_j^2 \,/\, \sum_1^2 r_j = 0.9 \,.$$

Next, we determine two angles θ_1 and θ_2 which determine two saddle parts, into which (together with convex ones) the EHD can be divided in the process of evaluation of the geometric quantities according to Connolly[13,14] (Fig. 1). Angles θ_1 and θ_2 follow from the relation $\sin\theta_i = l_i/r_i$ and $l_1 + l_2 = l$.

For the convex parts of the EHD surface area, S_c, it holds true

$$S_c = 2\pi[r_1^2(1+\sin\theta_1) + r_2^2(1+\sin\theta_2)] \tag{7}$$

whereas the saddle parts S_{sd} contribute by

$$S_{sd} = 2\pi r_p\left[\int_0^{\theta_1}(X_{ij} - r_p\cos\gamma)\mathrm{d}\gamma + \int_0^{\theta_2}(X_{ij} - r_p\cos\gamma)\mathrm{d}\gamma\right] =$$

$$= 2\pi r_p[(1+r_p)(\theta_1+\theta_2)\cos\theta_1 - r_p(\sin\theta_1 + \sin\theta_2)] \tag{8}$$

(X_{ij} stands for the height of the triangle). The reduced EHD surface area, $S^* = S/(\pi\sigma^2)$ (with respect to the diameter of hard sphere A) reads as

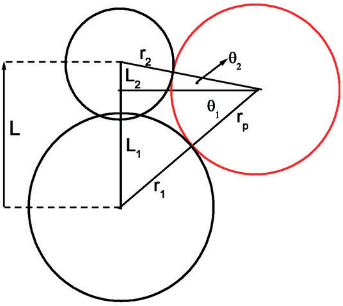

FIG. 1
Geometry of the heteronuclear hard dumbbell. Black line, HHD composed of sites with diameters σ_1, σ_2, site separation L; red line, probe sphere with radius r_p*, and characteristic angles of the saddle parts θ_1, θ_2

$$S^* = (S_c + S_{sd})/\pi\sigma^2 =$$
$$= \frac{1}{2}[(1+p^2) + (\sin\theta_1 + p^2\sin\theta_2) - r_p{}^{*2}(\sin\theta_1 + \sin\theta_2) +$$
$$+ r_p{}^*(1 + r_p{}^*)(\theta_1 + \theta_2)\cos\theta_1] \tag{9}$$

where $p = r_2/r_1$ and $r_p{}^* = r_p/r_1$. Taking derivatives of (*7*) and (*8*) with respect to r_1, r_2 and r_p, one obtains the reduced mean radius, $R^* = R/(\sigma/2)$

$$R^* = \frac{1}{2}[(1+p) + (\sin\theta_1 + p\sin\theta_2) + r_p{}^*(\sin\theta_1 + \sin\theta_2) -$$
$$- (1 + r_p{}^*)(\theta_1 + \theta_2)\cos\theta_1 / 2]\,. \tag{10}$$

Volumes of the convex and saddle parts follow from expressions

$$V_c = 2\pi/3\sum r_i^3(1 + \sin\theta_i + \cos^2\theta_i\sin\theta_i/2)$$

and

$$V_{sd} = 2\pi r_p^2\sum\int_0^{\theta_i}(X_{ij} - r_p\cos\gamma)^2\sin\gamma\,\mathrm{d}\gamma\,.$$

The reduced volume, $V^* = (V_\mathrm{c} + V_{sd})/(\pi\sigma^3/6)$ is

$$V^* = \frac{1}{2}[(1 + \sin\theta_1 + \cos^2\theta_1\sin\theta_1/2) + p^3(1 + \sin\theta_2 + \cos^2\theta_2\sin\theta_2/2)] +$$
$$+ \frac{3}{4}r_p{}^*(1 + r_p{}^*)\cos\theta_1[(1 + r_p{}^*)\cos\theta_1(\sin\theta_1 + \sin\theta_2) - r_p{}^*(\cos\theta_1 + \cos\theta_2)] +$$
$$+ \frac{1}{4}r_p{}^{*3}[(\cos^2\theta_1\sin\theta_1 + \cos^2\theta_2\sin\theta_2) + 2\sin\theta_1 + 2\sin\theta_2] -$$
$$- \frac{3}{4}r_p{}^{*2}(1 + r_p{}^*)\cos\theta_1(\theta_1 + \theta_2)\,. \tag{11}$$

The reduced quantity Q^* (for which holds true the inequality $S^* < Q^* < R^{*2}$) was in this study approximated by Eq. (*12*)

$$Q^* = S^*(R^{*2}/S^*)^{\delta} \tag{12}$$

found from the analysis of the third virial coefficients with $\delta = 1/2$, cf. ref.[15]. Then the non-sphericity parameters of pure HDs result from the values of the reduced quantities, i.e. $\alpha = R^*S^*/V^*$ and $\beta = Q^*S^{*2}/V^{*2}$.

The hard planar wall can be interpreted as a part of a hard sphere with the diameter tending to infinity. The geometric properties of hard planar wall, R_w, S_w, V_w, Q_w are consequently defined as those of a special planar circle with zero values of R_w and V_w and with surface area of a circle (its normal coincides with that of the hard wall) i.e. $S_w = 4\pi r_w^2$; $r_w = (r + r_p)\cos\theta$. (In the case of HD in its parallel orientation to a planar body an overlap of several circles is considered.)

Geometric Quantities of the Combined Bodies

As discussed previously, the background correlation function, Y, can be evaluated on the basis of ΔR^*, ΔS^*, ΔQ^*, ΔV^*, etc. Thus, geometric quantities of the combined body $R^{\mathrm{CB}*}$, $S^{\mathrm{CB}*}$, etc. have to be determined. For the pure HHD–wall system we need in principle the geometric quantities of CBs for different orientations of HHD with respect to the wall plane. Here we will consider only the perpendicular orientation, with larger or smaller site closer to the wall. In the case of the perpendicular orientation of HHD and site A (with diameter $\sigma_A = 1$) closer to the wall, we can calculate S^{CB} as surface area of HHD minus convex part of site A for angles $(0,\theta)$ plus saddle part for angles $(0,\pi/2 + \theta)$ where $\theta = \arcsin[(z - r_p)/(1 + r_p)]$ and z is distance of the site A from the wall (Fig. 2a). Thus,

$$R^{\mathrm{CB}*} = R^* - (1 - \sin\theta)/2 + r_p^*(1 + \sin\theta)/2 - (1 + r_p^*)(\pi/2 + \theta)\cos\theta/4 \tag{13}$$

$$S^{\mathrm{CB}*} = S^* - (1 - \sin\theta)/2 + r_p^{*2}\,(1 + \sin\theta)/2 + r_p^*(1 + r_p^*)(\pi/2 + \theta)\cos\theta/2 \tag{14}$$

$$\begin{aligned} V^{\mathrm{CB}*} = V^* - \{&(1 - \sin\theta - \cos^2\theta\sin\theta/2) + \\ &+ 3r_p^*(1 + r_p^*)\cos\theta[(1 + r_p^*)\cos\theta(1 + \sin\theta) - \\ &- r_p^*\cos\theta\sin\theta]/2 + r_p^{*3}(\cos^2\theta\sin\theta/2 + \sin\theta + 1) - \\ &- 3r_p^{*2}(1 + r_p^*)\cos\theta(\pi/2 + \theta)/2\}/2\,. \end{aligned} \tag{15}$$

These expressions are valid for the wall–site distances, z, where $\cos\theta \le r_p/(1 + r_p)$. For larger values of z we have to consider – instead of integrals from 0 to θ – integrals from ϕ to θ, where ϕ is given by the crossing of the probe sphere with the wall–site A line.

The differences in the geometric functionals, ΔR^*, ΔS^*, ΔQ^* and ΔV^* possess the following form

$$\Delta R^* = 1 - R^{\mathrm{CB}*}/R^* \tag{16}$$

$$\Delta S^* = 1 + [\cos\theta\,(1+r_p{}^*)/2]^2/S^* - S^{\mathrm{CB}*}/S^* \tag{17}$$

$$\Delta V^* = 1 - V^{\mathrm{CB}*}/V^* \tag{18}$$

$$\Delta Q^* = 1 - Q^{\mathrm{CB}*}/Q^* \,. \tag{19}$$

Substitution of the above expressions into (*6*) (with $v = y$, y being the packing fraction of pure HHDs) one can evaluate the pair wall–site correlation function for the perpendicular HHD orientation, with the large site A closer to the wall. When considering the reverse orientation (smaller site B closer to the plane) we have to realize that due to relation $r_2 << r_p$ the probe sphere contacts firstly (for small distances z) site A and only for $z > r_p/2$ site B (with the smaller radius r_2). In the latter case

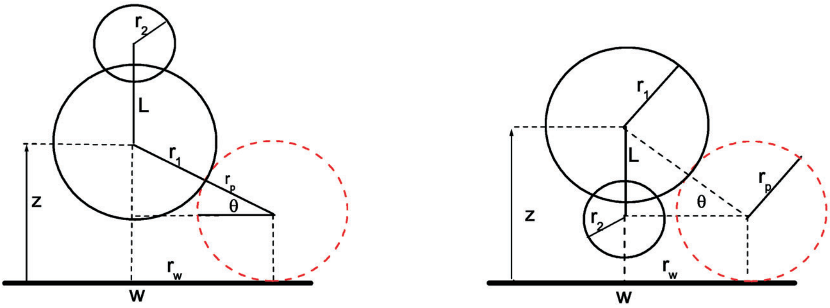

FIG. 2
a Geometry of heteronuclear hard dumbbell (in perpendicular orientation, larger site A closer to the wall). Red circle, probe sphere; θ, characteristic angle; z, distance of hard dumbbell from the hard wall (w). b The same as in Fig. 2a but for smaller site B closer to the wall

$$R^{\mathrm{CB}*} = R* - p(1-\sin\theta)/2 + r_p*(1+\sin\theta)/2 - (p+r_p*)(\pi/2+\theta)\cos\theta/4 \qquad (20)$$

$$S^{\mathrm{CB}*} = S* - p^2(1-\sin\theta)/2 + r_p*^2(1+\sin\theta)/2 + r_p*(p+r_p*)(\pi/2+\theta)\cos\theta/2 \qquad (21)$$

$$\begin{aligned} V^{\mathrm{CB}*} = V* - \{&p^3(1-\sin\theta+\cos^2\theta\sin\theta/2) + \\ &+ 3r_p*(p*+r_p*)\cos\theta[(p+r_p*)\cos\theta(1+\sin\theta) - \\ &- r_p*\cos\theta\sin\theta]/2 + r_p*^3(\cos^2\theta\sin\theta/2+\sin\theta+1) - \\ &- 3r_p*^2(p*+r_p*)\cos\theta(\pi/2+\theta)/2\}/2\,. \end{aligned} \qquad (22)$$

The average wall–site A correlation function $\bar{g}$ can be obtained from g_{WA} by considering all the acceptable orientations of site B with respect to the normal of the wall versus all possible HHD orientations.

Approximately Equimolar Hard Sphere–Heteronuclear Hard Dumbbell Mixtures Near a Hard Wall

Solutions of hard spheres with heteronuclear hard dumbbells represent the reference system for some realistic mixtures. In the literature one can find results of the MC studies of HHD mixtures performed by Archer et al.[16], Gulati and Hall[17] or Nezbeda et al.[18]. The paper by Nezbeda et al. brings distribution functions of HS and HHD near the planar wall for several concentrations of HS and several densities. Here we will consider approximately equimolar mixture at the highest density $v = 0.407$ and non-equimolar mixtures with mole fractions of HS equal to 0.271 and 0.725 at $v = 0.407$ or 0.410.

In our previous paper we studied pair distribution functions in ternary HS systems and found that a fair description of the effect of the third component on the dependence of g_{ij} on distance z_{ij} consists in proper choice of the radius (diameter) of the probe sphere. The best results were obtained for the weighted average of $\sigma_p = \sum x_i\sigma_i^2/\sum x_i\sigma_i$. As in ref.[18] the HS diameter is equal to the diameter of the larger site ($\sigma_{\mathrm{A}} = 1$) and σ_p of pure HHD equals 0.9, the probe diameter in the equimolar mixtures is $\sigma_p = 0.95$. This value was used here for evaluation of the wall–site A distribution functions. Beside this, values of the non-sphericity parameters α_s and β_s change slightly to smaller values with the increasing concentration of HS.

RESULTS

Our theoretical approach was applied to determine distribution functions of the HHD ($\sigma_1 = 1$, $\sigma_2 = 0.5$, site separation L = 0.625) near the planar wall; we calculate g_{WA} or g_{WB} for HHD in direction of the normal of the plane, with the larger site A or smaller site B closer to the wall. The average correlation function $\bar{g}_{WI}$ follows from g_{WI} by considering the ratio of all the acceptable orientation to all of them ($\int_\phi^{\pi/2} \mathrm{d}\sin\gamma / \int_{-\pi/2}^{\pi/2} \mathrm{d}\sin\gamma$). Theoretical dependence of g (dashed) and $\bar{g}$ (full line) on the reduced distance of the site center from the wall, z/σ, are presented in Figs 3 and 4 and compared with the MC data[18]. These are extracted from the relatively small figures in ref.[18] with approximate error 0.1 (max ≈ 0.25 for $z \approx z_{\min}$). In Fig. 3, theoretical dependence of g *vs* z^* is compared with simulation results for packing fraction $y = 0.308$. We take value $\sigma_p = 0.9$ (obtained as a weighted average from σ_1 and σ_2). A fair agreement of the calculated curve with MC data was found. The theoretical curve indicates also a cusp at distance $z^* \approx 0.875$. In Fig. 4, we compare the average correlation function, $\bar{g}_{WB}$, for the same packing fraction and σ_p as above. Agreement with MC data in this case is only qualitative; slightly better agreement can be obtained for $\sigma_p = 0.8$. This indi-

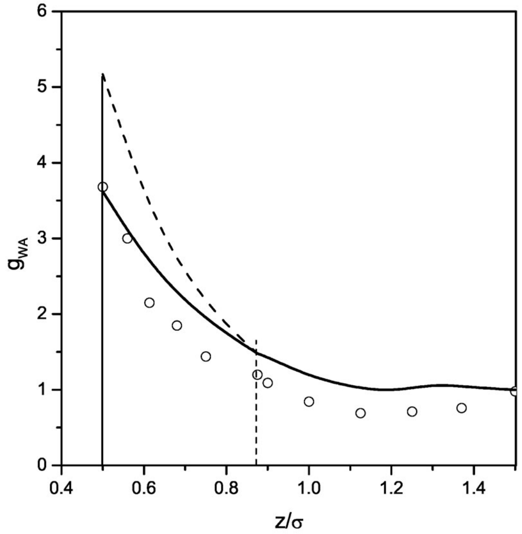

FIG. 3

Average correlation function (W–A) for the perpendicular orientation and larger site A closer to the wall, g_{WA} (full line) and radial distribution function for perpendicular orientation of HHD (dashed line); ○, MC data for $y = 0.306$

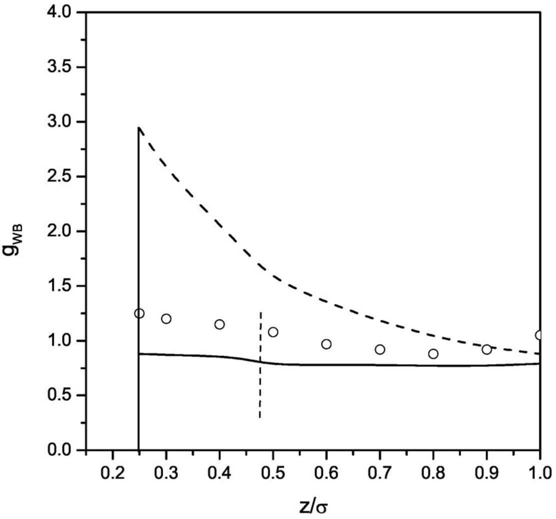

FIG. 4
The same as in Fig. 3 but for the smaller site B closer to the wall, g_{WB}

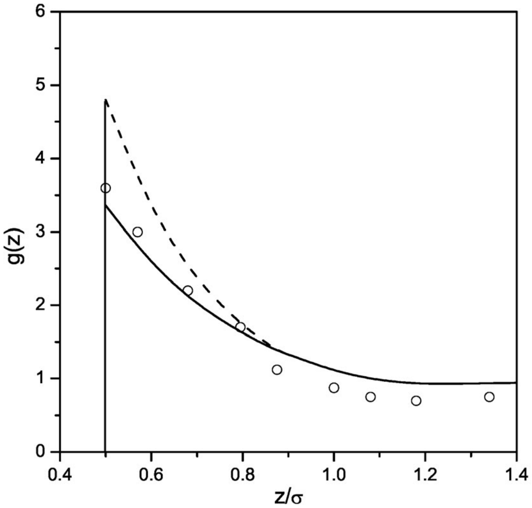

FIG. 5
Average correlation HHD/wall function $\bar{g}$ (larger site A closer to the wall) at packing fraction ν = 0.407 for approximately equimolar mixture of HS + HHD near a wall (full line) and radial distribution function for the perpendicular orientation of HHD (dashed line)

cates the fact that in the case of $\bar{g}_{WB}$ the evaluation of σ_p is more complicated than in the case of $\bar{g}_{WA}$: for small values of z/σ the contact of two B sites can be realized (it contributes by a large value to g), whereas the averaged value, σ_p, does not allow to consider such a contact at all. We did not discuss parallel orientation of HHD/wall, as we are not aware of any MC study for this orientation. Moreover, projection of the parallel HHD on the plain, important for the determination of ΔR, etc.) differs only slightly from that for single site A.

Next, we consider the HS + HHD mixtures near a wall. Because of the special choice of the HS diameter, $\sigma_s = \sigma_A$, we can simply modify the way of evaluation of R_{ref}, S_{ref}, etc., and ΔR^*, ΔS^*, ΔQ^* and ΔV^* discussed above; the effect of an addition of HSs consists mainly in change of the probe diameter. For the approximately equimolar mixture the accepted value was $\sigma_p = 0.95$.

Radial distribution function as well as average correlation function in the equimolar mixture for HHD/wall, g_{WA}, at the packing fraction $v = 0.407$ as obtained from the above expressions for a mixture, is presented in Fig. 5. Theoretical dependence is compared with the MC data and a fair agreement was found. In Fig. 6, the average correlation functions are depicted for the

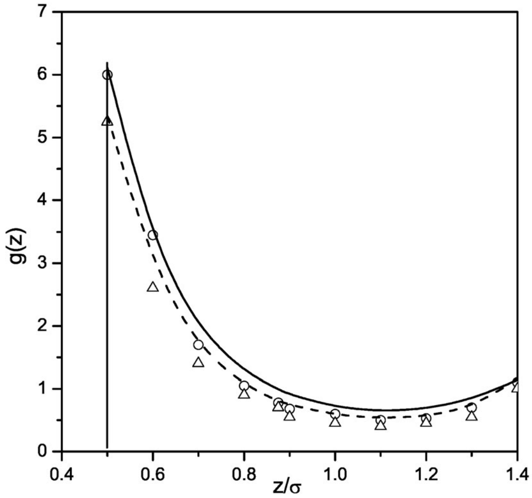

FIG. 6
The same as in Fig. 5 but for non-equimolar mixtures of HS + HHD at $v = 0.407$, $x_1 = 0.271$ and $v = 0.410$, $x_1 = 0.725$

same packing fraction and two values of the mole fraction (of HS), x_1 = 0.271 and 0.725. One can see that also the average correlation function $\bar{g}_{\mathrm{WA}}$ for non-equimolar concentrations compares well with the respective simulation data (presented in ref.[18] for $\nu = 0.407$).

From these figures a fair agreement is apparent. Comparison of Figs 5 and 3 indicates the fact that – due to a small difference of σ_p's for pure HHD and mixture – both the distribution functions are very similar.

The wall–site B distribution function of the mixture was not determined, because of problems with application of the "mixing rule" for σ_p needed in the initial part of the g_{WB} curve.

CONCLUSION

The study of the heteronuclear hard dumbbell represents a continuation of our systematic application of the theoretical method, proposed by us, to determine distribution functions and/or density profiles of homogeneous and heteronuclear hard body–wall systems on the basis of the residual chemical potentials of the considered pair of bodies and the respective combined body. The study of the heteronuclear hard dumbbell with considerably different sites indicates new questions, not present in the case of homonuclear dumbbells; simple approximations were used and some possible ways of improvements are indicated.

The present method leads to very simple relations even in the case of more complex systems – still in terms of differences in the geometric quantities, such as volume, surface area or mean radius of the studied molecules, inclusive those for a hard plane. The introduction of the enlarged fused hard sphere molecules (such as enlarged dumbbells) has improved the physical background of evaluation of the considered geometric quantities and enabled an extension of application of the method to more complex systems, such as hard bodies in a pore, hard bodies near different types of walls, dumbbells with different site separations (not only with tangent sites), triatomics and different heteronuclear fused hard sphere bodies. Besides of simplicity, also the fact that no input results for the bulk phase is expected, belongs to advantages of the method. The main disadvantage of the method consists in the limited range of distances $z/\sigma \in (1,2)$, where the method yields distribution functions. The upper limit of the range – in absence of understanding to the physical nature of the geometric quantity, Q – is due to the used approximation (for non-convex hard bodies). However, it is fair to say, that the available range is the most interesting one, e.g. for characterization of adsorption or molecule structures in nanotubes and biomolecules.

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