RADIAL DISTRIBUTION FUNCTION IN THE HARD SPHERE MIXTURES

Tomáš BOUBLÍK[a,b]

[a] Department of Chemistry, J. E. Purkinje University, 400 96 Ústí nad Labem, Czech Republic;
e-mail: boublik@sci.ujep.cz

[b] Department of Physical and Macromolecular Chemistry, Faculty of Science, Charles University,
128 43 Prague 2, Czech Republic

Dedicated to Professor William R. Smith on the occasion of his 65th birthday.

Equilibrium structures of both homogeneous and heterogeneous systems are, within statistical thermodynamics, characterized by distribution functions. Using the approach proposed recently – based on the determination of the cavity functions for the pair of hard spheres (HS) and the combined body – we studied the effect of different choices of the probe HS (which determines the shape of the combined hard body – enlarged dumbbell) on the prediction of the distribution functions in binary mixtures of HS with the aspect ratio 0.9, ternary mixtures with diameter ratios 1, 0.6 and 0.3, and density profiles of HS mixture with the aspect ratio 2 near a hard wall. It was found that the method, that uses the average geometric functionals determined for the probe HS with individual diameters multiplied by the respective mole fractions yields better results than the approaches based on average probe diameters.

Keywords: Distribution function; Density profile; Hard sphere mixture; Hard sphere near a hard wall; Binary systems; Ternary systems; Enlarged hard dumbbell; Hard sphere chemical potential; Probe diameter; Phase equilibria; Thermodynamics.

The knowledge of the structure of homogeneous fluids characterized by radial distribution functions (rdf) plays an important role in the prediction of the P-V-T behavior of fluids as well as phase equilibria. In the case of systems of hard spheres (HS) near a hard wall, HS in a planar slit or in spherical pore, the density profiles (dp) provide similar structure characteristics for studies of the P-V-T and thermodynamic behavior in inhomogeneous systems. Information on rdf or dp follows from simulation studies[1–9]. At low densities both the rdf and dp can be obtained from virial expansions; at higher densities solution of the Ornstein–Zernike (OZ) integral equation[2,10] and – more recently – density functional theory[11–14] (DFT) are the accurate

approaches to determine the structure characteristics of the above mentioned systems. Both the OZ and DFT approaches are quite versatile. However, often some initial information is needed and numerical solutions are essential for these methods. These disadvantages do not occur in the geometrical method considered by us recently, where rdf or df are determined from the relation between the background (cavity) correlation function, *Y*, and residual chemical potentials of pairs of HS and the corresponding combined body, i.e. a hard dumbbell[15,16]. The approach is so far limited to hard body fluids; it is rather simple and the recent version[17,18] (which employs the enlarged hard dumbbell (EHD)) makes it possible to describe equilibrium structure of both homogeneous and heterogeneous systems, pure fluids as well as mixtures in a simple way. Especially in the case of complex mixtures, simplicity and readiness of the evaluation of *Y* or *g* is very important. Actually, the residual chemical potential of the hard body depends practically only on the geometric characteristics – volume, surface area, mean radius, etc. – of the considered pair of HS and the corresponding combined hard body.

The geometric characteristics of the combined hard body, i.e. EHD (which originates when the probe is rolled over a hard dumbbell) depend on the HS diameters and also on the diameter of the probe. The choice of the probe diameter in the case of pure fluids, where the combined body is just an enlarged homogeneous dumbbell, is unambiguous – it is equal to the HS diameter of the dumbbell. In the case of mixtures with the combined body equal to the enlarged heterogeneous dumbbell, different choices may be considered. In our previous study[19] we took the simplest mixing rule $\sigma_{probe} = \Sigma x_i \sigma_i$. A study of several ways of determining the geometric functionals of the combined bodies in HS mixtures is the subject of the present study.

THEORETICAL

Evaluation of the rdf is based on the relation[15,16] between the background correlation function Y (= $g \exp [u(r)/kT]$, where u stands for the pair potential, k is the Boltzmann constant, T temperature, and g radial distribution function) and the residual chemical potentials $\Delta\mu_i$ of single HS and those for the combined hard body – hard dumbbell, $\Delta\mu_{ij}^{hd}$,

$$\ln Y = (\Delta\mu_i + \Delta\mu_j - \Delta\mu_{ij}^{hd})/kT . \tag{1}$$

In the case of hard bodies, rdf equals the background correlation function for all the distances of HS larger than the contact distance; for shorter distances Y is related to the correlation function, c.

The residual chemical potential can be expressed[20] as

$$\Delta\mu/kT = -\ln(1-y) + \left[\frac{y}{(1-y)}\right][3(R^*+S^*)+V^*] + \\ + \left[\frac{y}{(1-y)}\right]^2\left[\frac{3}{2}Q^*+3S^*+3V^*\right] + \left[\frac{y}{(1-y)}\right]^3\left(\frac{6-y}{3}\right)V^*.$$

(2)

The reduced geometric functionals of the pure hard sphere fluids with the HS diameter σ, $R^* = 2R/\sigma$, $S^* = S/\pi\sigma^2$, $Q^* = 4Q/\sigma^2$ and $V^* = 6V/\pi\sigma^3$, are all equal to one. (Here V, S, R stand for volume, surface area and the mean curvature integral divided by 4π; Q characterizes overlap of three particles, $R^2 > Q > S/4\pi$.) In the case of mixtures $R_i^* = p_i$, $S_i^* = Q_i^* = p_i^2$, $V_i^* = p_i^3$ where $p_i = \sigma_i/\sigma^o$ and σ^o is the reference HS diameter.

The geometric characteristics of the combined hard body – EHD – depend on p_i's and also on the diameter of the probe hard sphere, p_p. For the enlarged homonuclear dumbbell, p_p is equal to the diameter of the studied hard sphere, i.e. $\sigma_p = \sigma = \sigma^o$. If l (= L/σ) stands for the reduced center-to-center distance of the pair of molecules and arcsin $\theta = l/2$, then, for $l \leq \sqrt{3}$ (refs[21,22])

$$V^* = 1 + 3l - l^3/2 - 3\theta\cos\theta$$

(3)

$$S^* = 1 + 2\theta\cos\theta$$

(4)

and

$$R^* = 1 + l - \theta\cos\theta.$$

(5)

For l from the interval ($\sqrt{3}$, 2) the enlarged body is discontinuous (Fig. 1). It is then necessary to add contributions δV^*, δS^* and δR^* to volume, surface area and mean radius, namely

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

$$\delta S^* = -2\,\phi\cos\theta + \sin\phi$$

$$\delta R^* = -\sin\phi$$

where the angle ϕ follows from relation $\cos\phi = 2\cos\theta$.

The remaining geometric functional, Q, is related to the overlap of three HS's. It has the dimension $[l^2]$ and values $R^2 \le Q \le (S/4\pi)$.

For prolate spherocylinders (PSC),

$$Q = (S/4\pi)\xi \quad \text{where} \quad \xi = (4\pi R^2/S)^{1/2} \ . \tag{6}$$

In the case of EHD's, parameter Q is smaller than that of the corresponding PSC; we assume $Q = (S/4\pi)\xi^m$ with $m = 1/2$.

Geometric quantities in mixtures, R_{ij}^*, S_{ij}^* and V_{ij}^*, are extensions of relations for pure fluids. Thus

$$R_{ij}^* = \frac{1}{2}[\,p_i(1+\sin\theta_i) + p_j(1+\sin\theta_j)] - \frac{1}{4}(p_i + p_{\mathrm{p}})(\theta_i + \theta_j)\cos\theta_i +$$
$$+ \frac{1}{2}\,p_{\mathrm{p}}(\sin\theta_i + \sin\theta_j) + \frac{1}{2}\,p_{\mathrm{p}}\,\phi\cos\phi - p_{\mathrm{p}}\sin\phi \tag{7}$$
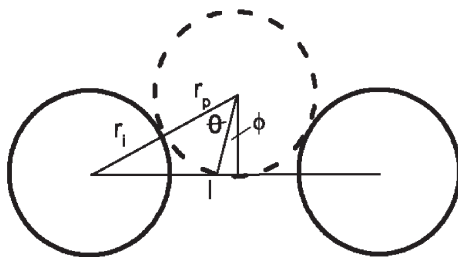
FIG. 1

Geometry of the EHD for distance $l > \sqrt{3}$. r_i and r_{p} stand for radii of a HS i and a probe, respectively; θ and ϕ are angles, l is pair distance

$$S_{ij}^* = \frac{1}{2}[p_i^2(1+\sin\theta_i) + p_j^2(1+\sin\theta_j)] + \frac{1}{2}p_p(p_i+p_p)(\theta_i+\theta_j)\cos\theta_i -$$
$$- \frac{1}{2}p_p^2(\sin\theta_i+\sin\theta_j) - p_p^2\phi\cos\phi + p_p^2\sin\phi \tag{8}$$

$$V_{ij}^* = \frac{1}{2}[(p_i^3+p_j^3) + (p_i^3+p_p^3)\sin\theta_i + (p_j^3+p_p^3)\sin\theta_j] +$$
$$+ \frac{1}{4}(p_i+p_p)^3\sin\theta_i\cos^2\theta_i + \frac{1}{4}(p_j+p_p)^3\sin\theta_j\cos^2\theta_j - \tag{9}$$
$$- \frac{3}{4}p_p^2(p_i+p_p)(\theta_i+\theta_j)\cos\theta_i - \frac{1}{2}p_p^3\sin\phi\cos^2\phi + \frac{3}{2}p_p^3\phi\cos\phi - p_p^3\sin\phi .$$

In Eqs (7)–(9)

$$p_p = \sigma_{probe}/\sigma^o$$

$$(p_i+p_p)\cos\theta_i = (p_j+p_p)\cos\theta_j = p_p\cos\phi$$

$$\theta_i = \arcsin l_i$$

where

$$l_i = [(p_i+p_p)^2 - (p_j+p_p)^2 + 4l^2]/8l .$$

Geometric quantity Q_{ij}^* follows from Eq. (6). The reduced differences ΔR^*, ΔS^*, ΔQ^* and ΔV^* are defined as

$$\Delta X^* = (X_i^* + X_j^* - X_{ij}^*)/\sum x_i p_i^n \tag{10}$$

with $n = 1$ for ΔR^*, $n = 2$ for ΔS^* or ΔQ^* and $n = 3$ for ΔV^*.

Geometric quantities in the inhomogeneous system of HS near a hard wall possess similar forms[18],

$$R_i^* = \frac{1}{2}[(p_i+p_p)(1+\sin\theta_i) - \frac{1}{2}(p_i+p_p)(\pi/2+\theta_i-2\phi)\cos\theta_i +$$
$$+ \pi/2(p_i+p_p)\cos\theta_i] - p_p\sin\phi \tag{11}$$

$$S_i^* = \frac{1}{2}[(p_i^2 - p_p^2)(1 + \sin\theta_i) + p_p(p_i + p_p)(\pi/2 + \theta_i - 2\phi)\cos\theta_i +$$

$$+ \frac{1}{2}(p_i + p_p)^2 \cos^2\theta_i + 2p_p^2 \sin\phi] \tag{12}$$

$$\Delta V_i^* = \frac{1}{2}\{(p_i^3 - p_p^3) - (p_i^3 - p_p^3)\sin\theta_i + \frac{3}{2}p_p^2(p_i + p_p)(\pi/2 + \theta_i - 2\phi)\cos\theta_i -$$

$$- (p_i + p_p)^2 \cos^2\theta_i[(p_i + p_p)\sin\theta_i/2 - p_p\sin\phi + 3p_p/2] + 2p_p^3\sin\phi\}. \tag{13}$$

From Eqs (7)–(9) it is clear that the differences in volume, surface area and radius depend on the HS diameters of both the components, on their center–center distance and also on the probe diameter σ_p or p_p. In the old version of this theory[19], the combined hard bodies were considered to be independent of the composition of a given mixture. With the use of the EHD as a model of the combined body, the problem of a proper choice of $p_p = \sigma_{probe}/\sigma^o$ is not unambiguous. In our previous paper[20] we took the approximation $p_p = \Sigma x_i p_i$ (where x_i stands for the mole fraction of component i). This approximation has proved to yield a fair prediction of the distribution functions of mixtures of moderately different HS's or mixtures with prevailing concentration of one component. In the present study we consider mixtures of HS's highly different in their diameters and approximately evenly included in the system. With the idea of unequal effect of different HS probes (which are rolled over the given hard dumbbell) on the total geometric quantities of EHD, we introduce further approximations for σ_{probe}, namely

$$p_p = \sum w_j^{(n)} p_j \tag{14}$$

where $w_j^{(n)}$ stands for, e.g., the volume fraction, surface fraction, etc. (In all the cases $\sum w_j^{(n)} = 1$.)

$$w_i^{(n)} = x_i p_i^n / \sum x_j p_j^n, \quad n = 1, 2, 3 \quad (w_i^{(0)} = x_i). \tag{15}$$

Finally, one can determine geometric quantities for the individual probe diameters $\sigma_{probe} = \sigma_i$, $i = 1, 2, 3, \ldots$ and take an average of the obtained val-

ues of R_{ij}, S_{ij}, V_{ij}, Q_{ij}. Equivalent to this averaging is the approach of taking average of $\ln Y_{ij}(p_k)$,

$$\ln Y_{ij} = \sum_k x_k \ln Y_{ij}(p_k) \,. \tag{16}$$

Investigation of the above mentioned rules is the objective of the following section.

RESULTS

In this study we consider first an equimolar binary mixture of HS of diameters 1 and 0.9 at packing fraction $y = 0.49$. This system was studied experimentally by Lee and Levesque[23]. The results obtained for the contact values of distribution functions, g_{ij}, are listed in Table I for all the above mentioned mixing rules; values of p_p are also included. From Table I it is clear that, due to relatively small difference in the diameters, differences in the calculated contact values of all g_{ij} are not significant. Thus, the application of the simplest rule – used in our previous study[18] – appears to be legitimate.

Next we considered two ternary systems of HS's with $\sigma_1 = 1$, $\sigma_2 = 0.6$ and $\sigma_3 = 0.3$, with the packing fraction $y = 0.4$, in one case with mole fractions $x_1 = x_2 = x_3 = 1/3$, in the other $x_1 = 1/6$, $x_2 = 1/3$ and $x_3 = 1/2$. The simulation studies are referred to in ref.[24]. Experimental values of the contact values of the distribution functions, g_{ij}, for all the pairs AA, BB, CC, AB, AC,

TABLE I
Contact values of the radial distribution functions of the binary hard sphere mixture with $\sigma_2/\sigma_1 = 0.9$, packing fraction $y = 0.49$ and mole fraction $x_1 = x_2 = 0.5$

Rule	σ_P	g_{AA}	g_{AB}	g_{BB}
MC	–	5.92	5.84	5.47
$p_\mathrm{p} = \Sigma x_i p_i$	0.950	5.82	5.64	5.46
$p_\mathrm{p} = \Sigma w_i^{(1)} p_i$	0.953	5.81	5.63	5.46
$p_\mathrm{p} = \Sigma w_i^{(2)} p_i$	0.955	5.80	5.62	5.45
$\Sigma x_i \ln g(p_i)$	–	5.82	5.63	5.46

and BC are listed in the first row of Table II. The next rows bring values of the rdf's determined for the probe diameter equal to: (i) $p_p = \sum x_i p_i$, (ii) $p_p = \sum w_i^{(1)} p_i = \sum x_i p_i^2 / \sum x_i p_i$, (iii) $p_p = \sum w_i^{(2)} p_i = \sum x_i p_i^3 / \sum x_i p_i^2$ and (iv) from an approximation $\ln g_{ij} = \sum x_k \ln Y_{ij}$ ($p_p = p_k$). (We did not consider volume fractions $w_i^{(3)}$.) For the pairs of largest and smallest molecules AA and CC, we determined the whole course of g_{ii} for the different above mentioned rules in the interval $x_{ii} \in (1, 2)$ (Figs 2 and 3). From the table and both the figures

TABLE II
Contact values of the radial distribution functions of the ternary hard sphere mixture with $\sigma_2/\sigma_1 = 0.6$, $\sigma_3/\sigma_1 = 0.3$, packing fraction $y = 0.40$ and mole fraction $x_1 = x_2 = x_3 = 1/3$

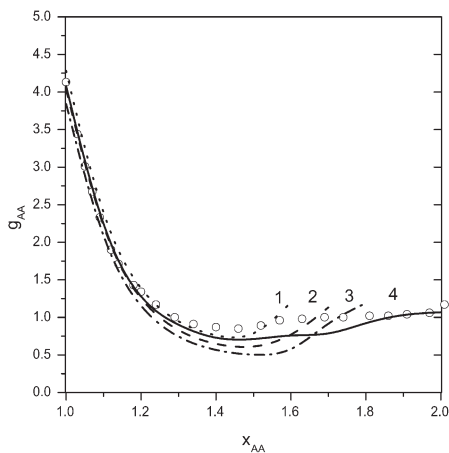| Rule	σ_P	g_{AA}	g_{BB}	g_{CC}	g_{AB}	g_{AC}	g_{BC}
MC	–	4.12	2.96	2.24	3.69	2.77	2.63
$p_p = \sum x_i p_i$	0.633	4.46	3.17	2.34	3.62	2.75	2.59
$p_p = \sum w_i^{(1)} p_i$	0.763	4.23	3.11	2.33	3.51	2.72	2.57
$p_p = \sum w_i^{(2)} p_i$	0.857	4.05	3.07	2.32	3.43	2.70	2.56
$\sum x_i \ln g(p_i)$	–	4.24	3.12	2.33	3.52	2.72	2.58

FIG. 2
Radial distribution function for a pair of the biggest HS, g_{AA} vs x_{AA}, in the ternary system of HS with diameter ratios 1, 0.6, 0.3 at packing fraction $y = 0.40$ and concentrations $x_1 = x_2 = x_3 = 1/3$. *1* for $p_p = \sum x_i p_i$, *2* for $p_p = \sum w_i^{(1)} p_i$, *3* for $p_p = \sum w_i^{(2)} p_i$, *4* for $\ln g = \sum x_i \ln Y(p_i)$

one can conclude that the simplest approximation, $p_p = \sum x_i p_i$, is insufficient and the resulting value of p_p too small; the use of the surface fractions seems most appropriate. The best overall results follow from the method of average logarithm, $\ln g_{ij} = \sum x_k \ln Y_{ij}(p_k)$.

In the case of the HS system with mole fractions $x_1 = 1/6$, $x_2 = 1/3$, $x_3 = 1/2$, the concentration of the largest HS is relatively small and p_p's determined from the different mixing rules are similar (and approaching $p_p = 0.5$). From Table III and Figs 4 and 5 (where $g_{AA}(x_{AA})$ and $g_{BC}(x_{BC})$ are depicted on the interval $x \in (1, 2)$), a fair prediction of g_{ij} from the approximation $\ln g = \sum x_i \ln Y(p_i)$ in the whole considered interval is apparent.

The last system studied was a binary hard sphere mixture near a hard wall. Density profiles of both the components, obtained by MC simulations in a system with the HS diameter ratio $\sigma_2/\sigma_1 = 2$, mole fraction $x_2 = 0.2$ and bulk density $\rho_b = 0.3209$ were published by Malijevský[14]. Molecules of the mixture components differ by an order of magnitude in their volumes; on the contrary, the mole fraction of the bigger HS is rather small so that different ways of determining p_p yield similar results. A comparison of the predicted and pseudo-experimental contact values of density of both the components is given in Table IV. This comparison reveals a fair prediction of the contact values of ρ_i when we approximated the probe diameter by
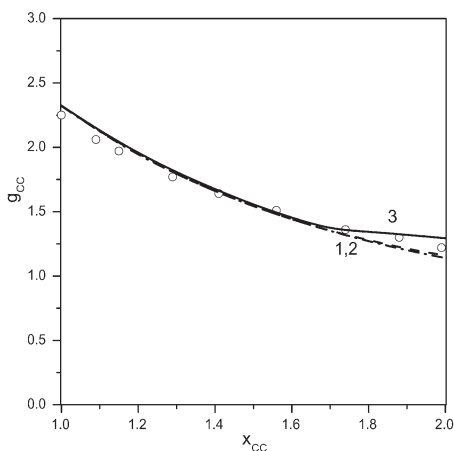

FIG. 3
Radial distribution function for a pair of the smallest HS, g_{CC} vs x_{CC}, in the ternary system of HS with diameter ratios 1, 0.6, 0.3 at packing fraction $y = 0.40$ and concentrations $x_1 = x_2 = x_3 = 1/3$. *1* for $p_p = \sum w_i^{(1)} p_i$, *2* for $p_p = \sum w_i^{(2)} p_i$, *3* for $\ln g = \sum x_i \ln Y(p_i)$
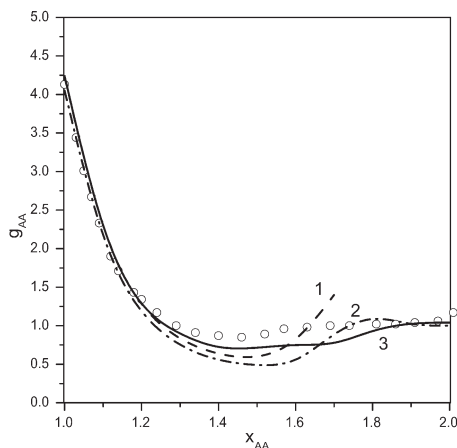
FIG. 4

Radial distribution function for a pair of the biggest HS, g_{AA} vs x_{AA}, in the ternary system of HS with diameter ratios 1, 0.6, 0.3 at packing fraction $y = 0.40$ and concentrations $x_1 = 1/6$, $x_2 = 1/3$, $x_3 = 1/2$ (only for approximation $\ln g = \sum x_i \ln Y(p_i)$)
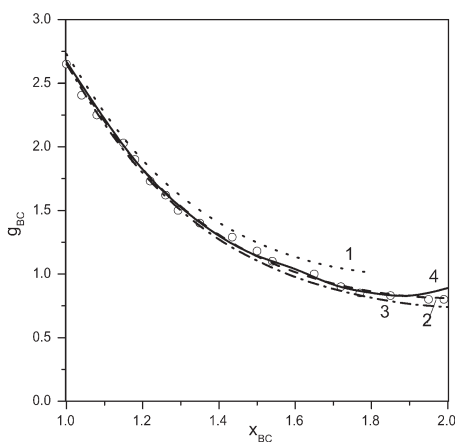

FIG. 5

Radial distribution function for a pair of smaller and smallest HS, g_{BC} vs x_{BC}, in the ternary system of HS with diameter ratios 1, 0.6, 0.3 at packing fraction $y = 0.40$ and concentrations $x_1 = 1/6$, $x_2 = 1/3$, $x_3 = 1/2$. 1 for $p_p = \sum x_i p_i$, 2 for $p_p = \sum w_i^{(1)} p_i$, 3 for $p_p = \sum w_i^{(2)} p_i$, 4 $\ln g = \sum x_i \ln Y(p_i)$

TABLE III
Contact values of the radial distribution functions of the ternary hard sphere mixture with $\sigma_2/\sigma_1 = 0.6$, $\sigma_3/\sigma_1 = 0.3$, packing fraction $y = 0.40$ and mole fraction $x_1 = x_2 = x_3 = 1/2$

Rule	σ_P	g_{AA}	g_{BB}	g_{CC}	g_{AB}	g_{AC}	g_{BC}
MC	–	4.54	3.17	2.32	3.69	2.77	2.63
$p_p = \Sigma x_i p_i$	0.517	4.91	3.40	2.43	3.93	2.91	2.73
$p_p = \Sigma w_i^{(1)} p_i$	0.642	4.55	3.31	2.42	3.58	2.81	2.67
$p_p = \Sigma w_i^{(2)} p_i$	0.760	4.17	3.22	2.41	3.44	2.77	2.65
$\Sigma x_i \ln g(p_i)$	–	4.61	3.34	2.43	3.80	2.87	2.71

TABLE IV
Contact values of the density profiles of the binary hard sphere mixture near a hard wall. $\sigma_2/\sigma_1 = 2$, mole fraction $x_2 = 0.2$ and $\rho_b = 0.3209$

Rule	σ_P	ρ_1	ρ_2
MC	–	0.67	1.18
$p_p = \Sigma x_i p_i$	1.2	0.59	1.21
$p_p = \Sigma w_i^{(1)} p_i$	1.333	0.49	1.14
$p_p = \Sigma w_i^{(2)} p_i$	1.500	0.37	1.06
$\Sigma x_i \ln g(p_i)$	–	0.54	1.18

the value $\sum x_i p_i$ and/or determined $\ln g$ as $\sum x_i \ln g(p_i)$. Whereas the contact values of ρ_2 with different choices of p_p change only marginally, ρ_1 decreases with the order of the fraction $w^{(i)}$ noticeably.

CONCLUSION

In this paper we have studied a simple geometric method to characterize structure of homogeneous and inhomogeneous hard sphere systems composed of two and more components. Such a method is important for several reasons: (i) it provides a deep insight into the way the HS structure is formed; (ii) for pure fluids even relatively complex methods of determining distribution functions/density profiles are tractable whereas extension of these methods to mixtures might be difficult and/or rather time-

consuming; (iii) simplicity and quick acquirement of the structure characteristics might be decisive for technical applications, such as applications in chemical technology, biochemistry or geology. The studied method possesses such a traits and yields a fair description of the fluid structure in the most important range of distances of HS pairs.

The use of the enlarged hard dumbbell model (instead of the standard HB) for the combined hard body makes it possible to apply some results of the convex body geometry and enables formulation of relationships for the geometric quantities in the case of inhomogeneous systems. Extension of such formulas to hard sphere mixtures is simple and straightforward. However, a problem arises with the choice of the diameter of a HS probe (= σ_{probe}, $p_p = \sigma_{probe}/\sigma^o$), which determines the shape of the enlarged hard body. From the present study it follows that simple prescription $p_p = \sum x_i p_i$ is sufficient in the case of mixtures whose HS diameters differ only slightly, or when the smaller HS's are more abundant. In other cases the use of the surface fractions instead of mole fractions yields better results. The method of determining of all the geometric quantities stepwise for all the different diameters (of the respective HS's) and their averaging, or – equivalently – averaging of the logarithm of the background correlation function, appears to be versatile and accurate. This approach is only slightly more laborious than methods with one probe diameter only.

Prediction of the dependence of the radial distribution function or density profile at distances beyond twice the HD diameter remains still an open problem, which is related to formulation of a suitable expression for the evaluation of geometric quantity Q. While in the case of PSC (corresponding in their shape to EHD) quantity Q in a relatively broad range is given by a constant ratio of powers of R and S, in the case of EHD Q varies (i.e. power m in the correction factor ξ^m) with the site–site distance l. We plan to deal with this problem in future.

SYMBOLS

g	radial distribution function
i, j, k	indices
k	Boltzmann constant
l	site–site distance
n	power
p_i	aspect ratio
Q	geometric quantity of dimension, l^2
R	mean radius, mean curvature integral/4π
R^*	reduced mean radius
S	surface area

S^*	reduced surface area
X^*	reduced geometric quantity
x_i	mole fraction
Y	background correlation function
y	packing fraction
V	volume
V^*	reduced volume
$w_i^{(2)}$	surface fraction
ΔX	difference in geometric quantities
$\Delta\mu$	residual chemical potential
ϕ	angle
μ	chemical potential
θ	angle
ρ	density
σ	diameter
ξ	ratio of geometric quantities

REFERENCES

1. Henderson J. R., Van Swol F.: *Mol. Phys.* **1984**, *51*, 991.
2. Zhou Y. Q., Stell G.: *Mol. Phys.* **1989**, *66*, 767.
3. Pospíšil R., Malijevský A., Jech P., Smith W. R.: *Mol. Phys.* **1993**, *78*, 1461.
4. Labík S., Smith W. R.: *Mol. Phys.* **1996**, *88*, 1411.
5. Smith W. R., Vörtler H. L.: *Mol. Phys.* **2003**, *101*, 805.
6. Peterson B. K., Gubbins K. E.: *Mol. Phys.* **1987**, *62*, 215.
7. Henderson J. R.: *Mol. Phys.* **1986**, *59*, 89.
8. Gelb L. D., Gubbins K. E.: *Phys. Rev. E* **1997**, *55*, R1290.
9. Trokhymchuk A., Henderson D., Sokolovski S.: *J. Phys. Chem. B* **1995**, *99*, 17059.
10. Snook I. K., Henderson D.: *J. Chem. Phys.* **1978**, *68*, 2134.
11. Münster A.: *Statistical Thermodynamics*, Vol. 1. Springer, Berlin 1969.
12. Rosenfeld Y., Tarazona P.: *Mol. Phys.* **1998**, *95*, 141.
13. Denton A. R., Ashcroft N. W.: *Phys. Rev. A* **1991**, *44*, 8242.
14. Malijevský A.: *J. Chem. Phys.* **2006**, *125*, 194519.
15. Meeron E., Siegert A. J. F.: *J. Chem. Phys.* **1968**, *48*, 3139.
16. Labík S., Malijevský A., Nezbeda I.: *Mol. Phys.* **1987**, *60*, 1107.
17. Boublík T.: *Mol. Phys.* **2006**, *104*, 3425.
18. Boublík T.: *J. Phys. Chem. C* **2007**, *111*, 15512.
19. Boublík T.: *Mol. Phys.* **1986**, *59*, 775.
20. Boublík T.: *Mol. Phys.* **2002**, *100*, 3443.
21. Connolly M. L.: *J. Appl. Crystallogr.* **1983**, *16*, 548.
22. Connolly M. L.: *J. Am. Chem. Soc.* **1985**, *107*, 1118.
23. Lee L. L., Levesque D.: *Mol. Phys.* **1973**, *26*, 1351.
24. Šindelka M., Boublík T.: *Fluid Phase Equilib.* **1998**, *143*, 13.