

## NEW APPROXIMATE ANALYTICAL FORMULA FOR THE SOLUTE–SOLVENT CONTACT DISTRIBUTION FUNCTION IN AN INFINITELY DILUTE BINARY HARD-SPHERE MIXTURE

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

A new analytical expression for the contact value of the solute–solvent pair distribution function of a binary hard-sphere mixture at infinite dilution is proposed, based on scaled-particle-theory-like arguments. For high solute–solvent diameter ratio it predicts perfect agreement with the simulation results.

**Keywords:** Thermodynamics; Structure prediction; Scaled-particle theory; Solutions; Solvents; Binary mixtures.

During the past several years, renewed interest has been focused on hard-sphere (HS) systems with large differences in their component diameters (see<sup>1–4</sup> and references therein). Such a system that is dilute with respect to the larger spheres can serve as a simple model of a colloidal suspension. The solute–solute and solute–solvent pair distribution functions are key quantities of interest, and their contact values yield the equation of state. One approach for obtaining analytical approximations for these contact values is based on various extensions of the scaled-particle theory of Reiss et al.<sup>5</sup> (e.g., refs<sup>4,6</sup>). In this note we develop a new analytical formula for the contact value of the solute–solvent pair distribution function at infinite dilution, employing ideas similar to those used in our previous work on a geometrically-based hierarchy of integral equations for HS systems<sup>6</sup>.

## THEORY

We consider a binary HS mixture, where the solvent corresponds to hard spheres of diameter  $\sigma_1 = 1$  and the solute to hard spheres of diameter  $\sigma_2 = d$ , which is at infinite dilution in the solvent. In this limiting case, the packing fraction of solute is

$$\eta_2 = \frac{\pi N_2 \sigma_2^3}{6 V} = \frac{\pi N_2 d^3}{6 V} = 0$$

and the overall packing fraction of the system is given by that of the solvent

$$\eta = \eta_1 = \frac{\pi N_1 \sigma_1^3}{6 V} = \frac{\pi N_1}{6 V}$$

where  $N_1$  and  $N_2$  are the numbers of spheres of solvent and solute, respectively, and  $V$  is the system volume.

The contact value of the solute-solvent distribution function at infinite dilution,  $g_{12}^\infty(d_{12})$ , can be expressed in terms of chemical potentials via<sup>7</sup>

$$\ln g_{12}^\infty(d_{12}) = \beta \mu_1^e(1) + \beta \mu_1^{e,\infty}(d) - \beta \mu_{12}^{e,\infty}(1,d) \quad (1)$$

where superscript  $e$  denotes an excess value,  $\infty$  denotes infinite dilution,  $\beta = 1/(kT)$ ,  $\mu_1^e(1)$  is the excess chemical potential of pure solvent spheres,  $\mu_1^e(d)$  is the excess chemical potential of a HS of diameter  $d$ , and  $\mu_{12}^{e,\infty}(1,d)$  is the excess chemical potential of the hard diatomic formed by two contacting spheres of diameters 1 and  $d$ .

The combination of the last two terms in Eq. (1) corresponds to the work needed to extract an imaginary solvent sphere (cavity) of diameter 1 from inside the larger sphere to a position at contact (Fig. 1). This work is given by

$$\beta w_{12}(1,d) = \beta \mu_{12}^{e,\infty}(1,d) - \beta \mu_1^{e,\infty}(d). \quad (2)$$

The work can be calculated in a way similar to that used in the BGY-like hierarchy of integral equations developed by us previously<sup>6</sup>:

$$\beta w_{12}(1,d) = 2\pi \int_0^d dx \int_{\cos\theta^*}^1 d(\cos\theta) \rho^{[3]}(x,\cos\theta) \cos\theta \quad (3)$$

where  $\rho^{[3]}(x, \cos\theta)$  is the conditional three-particle density function corresponding to a solute (1)–solvent cavity (2)–solvent particle (3) configuration, where the cavity is in contact with a solute particle 3 (see Fig. 1). The configuration of particles is described by the solute-cavity centre-to-centre distance  $x$ , which expresses the gradual emergence of the solvent cavity from the solute particle ( $x = 0$  corresponds to a fully submerged particle and  $x = 1$  to the pair in contact), and by the angle  $\theta$  between the vectors  $\vec{r}_{12}$  and  $\vec{r}_{23}$ . The lower integration limit  $\cos\theta^*$  in the inner integral occurs when particles 1 and 3 are in contact. For  $x \rightarrow 0$  the conditional density  $\rho^{[3]}(0, 1)$  becomes the contact value of the two-particle density  $\rho^{(2)}(d_{13}) \equiv \rho^{(2)}(d_{12})$ . Since particle 3 remains in contact with particle 2 for all configurations in Eq. (3), a not unreasonable approximation is that its value does not considerably differ from this limiting value.

On these grounds, Eq. (3) can be approximated by

$$\beta w_{12}(1, d) = \rho^{(2)}(d_{12}) \Delta V_{\text{excl}} \alpha \quad (4)$$

where  $\Delta V_{\text{excl}}$  is the increase in volume excluded to a sphere centre of particle 3 when particle 2 is fully emerged from particle 1, given by the difference between the excluded volumes of the contacting solute–solvent diatomic and solute particles:

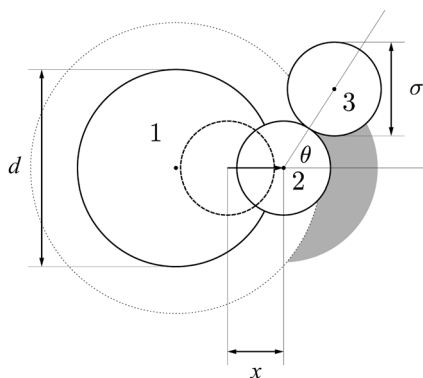


FIG. 1

Gradual emergence of a solvent particle (2) of diameter  $\sigma$  from a solute particle (1) with diameter  $d$ . The shadowed area corresponds to the maximum increase in excluded volume  $\Delta V_{\text{excl}}$  of Eq. (5)

$$\Delta V_{\text{excl}} = \frac{\pi}{6} \frac{7 + 4d}{1 + d}. \quad (5)$$

Since  $\rho^{(2)}(d_{12})$  is given by the contact value of solute–solvent pair distribution function, we have

$$\rho^{(2)}(d_{12}) = \rho g_{12}^{\infty}(d_{12}) \quad (6)$$

and we can thus write

$$\beta w_{12}(1, d) = \eta g_{12}^{\infty}(d_{12}) \frac{7 + 4d}{1 + d} \alpha. \quad (7)$$

The parameter  $\alpha$  depends on density and the solute diameter  $d$ . Equations (1), (2) and (7) may be combined to yield

$$\alpha = \frac{1 + d}{7 + 4d} \frac{[\beta\mu_1^e(1) - \ln(g_{12}^{\infty}(d_{12}))]}{\eta g_{12}^{\infty}(d_{12})}. \quad (8)$$

For low density,  $\alpha$  is equal to unity and for greater densities it decreases slowly.

Calculation of  $\beta\mu_1^e(1)$  requires knowledge of an equation of state of the pure HS fluid. We use here the simple but precise<sup>8</sup> equation of state due to Kolafa<sup>9</sup>

$$z = \frac{pV}{NkT} = \frac{1 + \eta + \eta^2 - 2/3\eta^3(1 + \eta)}{(1 - \eta)^3} \quad (9)$$

which gives the contact value for a pure fluid:

$$g_1(1) = \frac{1 - 1/2\eta + 1/12\eta^2 - 1/6\eta^3}{(1 - \eta)^3} \quad (10)$$

and the reduced excess chemical potential:

$$\beta\mu_1^e(1) = \frac{5}{3} \ln(1 - \eta) + \frac{\eta(58 - 79\eta + 39\eta^2 - 8\eta^3)}{6(1 - \eta)^3}. \quad (11)$$

Provided we know  $g_{12}^{\infty}(d_{12})$ , using Eqs (8) and (11), we can calculate values of  $\alpha$ . We can gain an idea of the expected behaviour of  $\alpha$  by using recently published simulation data<sup>4</sup>. In Fig. 2 we show results for  $\alpha$  for a wide range of diameters at the relatively high density  $\rho = 0.8$ . It can be seen that  $\alpha$  can be reasonably approximated by the simple linear formula

$$\alpha = a + b/d . \quad (12)$$

The parameters  $a$  and  $b$  can be obtained from two exact limiting conditions, valid for pure HS and for a HS at a hard wall, respectively:

$$g_{12}^{\infty}(d_{12}) = g_1(1) \quad (13)$$

and

$$\lim_{d \rightarrow \infty} g_{12}^{\infty}(d_{12}) = z . \quad (14)$$

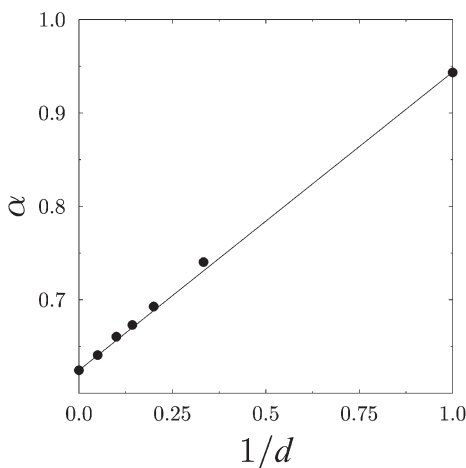


FIG. 2

Dependence of the parameter  $\alpha$  on the reciprocal diameter  $1/d$  at the density  $\rho = 0.8$ . Circles correspond to the values obtained from the simulation data of Viduna and Smith<sup>4</sup> and the line is the interpolation formula (12)

Using these conditions and the interpolation formula of Eq. (12), we may obtain an expression for  $g_{12}^\infty(d_{12})$ . Solving the previous set of equations we obtain

$$\ln g_{12}^\infty(d_{12}) = \beta\mu_1^e(1) + W\left(\frac{7 + 4d}{1 + d} \frac{8z[\beta\mu_1^e(1) - \ln(g_1(1))] - 11(1 - d)[\beta\mu_1^e(1) - \ln z]}{44zg_1(1)d} e^{\beta\mu_1^e(1)}\right) \quad (15)$$

where the Lambert function,  $W(x)$ , is the principal branch of the solution of the equation  $W(x)e^{W(x)} = x$  (ref.<sup>10</sup>).

### RESULTS AND DISCUSSION

In Fig. 3, we show the solute–solvent contact distribution function at infinite dilution as a function of the reciprocal solute diameter. The simulation data due to Viduna and Smith<sup>4</sup> are compared with several theoretical predictions. Two predictions use the same general formula:

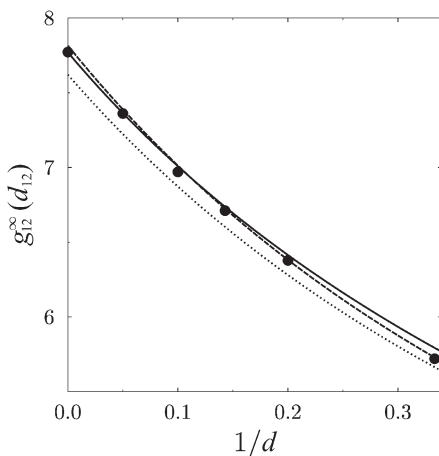


FIG. 3

Comparison of the solute–solvent contact distribution function in an infinitely dilute binary hard-sphere mixture at the density  $\rho = 0.8$ . The circles are the simulation data (Viduna and Smith<sup>4</sup>), the full line corresponds to our results of Eq. (15), the dashed line and dotted line were obtained from the eCS and BMCSL equations of state, respectively

$$g_{12}^{\infty}(d_{12}) = \frac{C_0 + C_1 d + C_2 d^2}{(1 + d)^2}. \quad (16)$$

The coefficients  $C_0$ ,  $C_1$  and  $C_2$  are given by the Boublík–Mansoori–Carnahan–Starling–Leland equation of state<sup>11,12</sup> (BMCSL)

$$C_0 = \frac{1}{1 - \eta} \quad (17)$$

$$C_1 = \frac{4 - 2\eta}{(1 - \eta)^2} + \frac{2 \ln(1 - \eta)}{\eta} \quad (18)$$

$$C_2 = \frac{-1 + 6\eta - 3\eta^2}{(1 - \eta)^3} - \frac{2 \ln(1 - \eta)}{\eta} \quad (19)$$

or by the extended Carnahan–Starling equation of state (eCS) due to Stantos et al.<sup>3</sup>

$$C_0 = \frac{4 - 3\eta}{6(1 - \eta)^2} - \frac{\ln(1 - \eta)}{3\eta} \quad (20)$$

$$C_1 = \frac{4(4 - 3\eta)}{3(1 - \eta)^2} + \frac{10 \ln(1 - \eta)}{3\eta} \quad (21)$$

$$C_2 = \frac{-4 + 17\eta - 9\eta^2}{2(1 - \eta)^3} - \frac{3 \ln(1 - \eta)}{\eta}. \quad (22)$$

The prediction obtained from BMCSL systematically underestimates the contact distribution function. The values obtained from eCS are in perfect agreement with the simulation data at moderate solute diameters  $d$  but slightly overestimate them at high diameters  $d$ . In this region our new formula (15) gives superior results; however, it overestimates the contact values at smaller diameters  $d$ .

We also examined the sensitivity of our approach to the precise form of Eq. (12), by trying other interpolating formulae which are nearly linear in  $1/d$  (e.g.,  $\alpha = (a + b/d)^{1/2}$ ), and to the precise form of the pure HS equation of state. We found the numerical results to be nearly independent of the approximations chosen.

The proposed method for calculation of  $g_{12}^{\infty}(d_{12})$  is based on the simplest (0-th order) term in the hierarchy of integral equations<sup>6</sup>. Higher-order terms may also be used, at the expense of more complicated calculations. In such a case, the resulting theory will probably give even more accurate results, and can also be used to calculate the solute–solute pair distribution function, which is a much more challenging problem than its solute–solvent counterpart and which is an object of much interest<sup>1</sup>.

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## REFERENCES

1. Henderson D., Trokhymchuk A., Woodcock L. V., Chan K. Y.: *Mol. Phys.* **2005**, *103*, 667.
2. Amokrane S., Ayadim A., Malherbe J. G.: *J. Chem. Phys.* **2005**, *123*, 174508.
3. Santos A., Yuste S. B., de Haro M. L.: *J. Chem. Phys.* **2005**, *123*, 234512.
4. Viduna D., Smith W. R.: *Mol. Phys.* **2002**, *100*, 2815.
5. Reiss H., Frisch H. L., Lebowitz J. L.: *J. Chem. Phys.* **1959**, *31*, 369.
6. Labík S., Malijevský A., Smith W. R.: *Mol. Phys.* **1994**, *83*, 983.
7. Labík S., Malijevský A., Nezbeda I.: *Mol. Phys.* **1987**, *60*, 1107.
8. Mulero A., Galan C., Cuadros F.: *Phys. Chem. Chem. Phys.* **2001**, *3*, 4991.
9. Kolafa J.: *Mol. Phys.* **1986**, *59*, 1035.
10. Corless R. M., Gonnet G. H., Hare D. E. G., Jeffrey D. J., Knuth D. E.: *Adv. Comput. Math.* **1996**, *5*, 329.
11. Boublík T.: *J. Chem. Phys.* **1970**, *53*, 471.
12. Mansoori G. A., Carnahan N. F., Starling K. E., Leland T. W.: *J. Chem. Phys.* **1971**, *54*, 1523.