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## First derivative of the hard-sphere radial distribution function at contact

David M Heyes<sup>1</sup>, Michael Cass<sup>1</sup>, Arkadiusz C Brańka<sup>2</sup> and Hisashi Okumura<sup>3</sup>

<sup>1</sup> Division of Chemistry, School of Biomedical and Molecular Sciences, University of Surrey, Guildford GU2 7XH, UK

<sup>2</sup> Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179 Poznań, Poland

<sup>3</sup> Department of Physics, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8602, Japan

E-mail: [d.hey@surrey.ac.uk](mailto:d.hey@surrey.ac.uk), [m.cass@surrey.ac.uk](mailto:m.cass@surrey.ac.uk), [branka@ifmpan.poznan.pl](mailto:branka@ifmpan.poznan.pl) and [hokumura@tb.phys.nagoya-u.ac.jp](mailto:hokumura@tb.phys.nagoya-u.ac.jp)

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### Abstract

Molecular dynamics simulations have been carried out of the radial distribution function of the hard sphere fluid for a range of densities in the equilibrium fluid and just into the metastable region. The first derivative of the hard-sphere radial distribution function at contact was computed and its density dependence fitted to a simple analytic form. Comparisons were made with semi-empirical formulae from the literature, and of these the formula proposed by Tao *et al* (1992 *Phys. Rev. A* **46** 8007) was found to be in best agreement with the simulation data, although it slightly underestimates the derivative at the higher packing fractions in excess of about 0.45. Close to contact, within a few per cent of the particle diameter, the radial distribution function can be represented well by a second order polynomial. An exponential function, which has some useful analytic features, can also be applied in this region.

A long-standing challenge of statistical mechanics is the prediction of the properties of a simple liquid for a given pair interaction,  $\phi(r)$ . As the structure of simple liquids is dominated by the intermolecular repulsive forces, a fluid of hard spheres is often used as a 'reference' fluid and the effects of particle softness and attractive forces treated by perturbation theory [1]. The hard sphere potential is

$$\phi(r) = \begin{cases} \infty, & r \leq \sigma \\ 0 & r > \sigma, \end{cases} \quad (1)$$

where  $\sigma$  is the hard sphere diameter. This potential is discontinuous at  $r = \sigma$ . The equation of state of the hard sphere fluid is a fundamental quantity for this study, which can be expressed

in terms of the compressibility factor,  $Z = P/\rho k_B T$  where  $k_B$  is Boltzmann's constant,  $T$  is the temperature and  $P$  is the pressure, and  $\rho = N/V$  is the number density for  $N$  hard spheres in volume  $V$ . The Carnahan and Starling (CS) formula [2] for  $Z$  is used here for incorporation in analytic expressions

$$Z(\zeta) = \frac{1 + \zeta + \zeta^2 - \zeta^3}{(1 - \zeta)^3} \quad (2)$$

where  $\zeta = \pi\rho\sigma^3/6$  is the packing fraction. The marginally more accurate Kolafa equation of state [3, 4] is used in conjunction with the simulation data

$$Z(\zeta) = \frac{1 + \zeta + \zeta^2 - 2(\zeta^3 + \zeta^4)/3}{(1 - \zeta)^3}. \quad (3)$$

In both cases the radial distribution function at contact of the spheres,  $g(\sigma)$  or simply  $g_0$  for conciseness, is given by  $g(\sigma) \equiv g_0 = (Z - 1)/4\zeta$  [1, 2].

Another quantity that occurs in perturbation and other theories of simple fluids and colloids using a hard sphere reference fluid is the slope of  $g(r)$  at contact,  $y_1$ , (e.g., see [5, 6]),

$$y_1(\zeta) \equiv \sigma \frac{d}{dr} g(r)|_{r=\sigma} \quad (4)$$

or  $y_1 \equiv g'$ . Unfortunately, an expression for  $y_1$  as a function of packing fraction is more difficult to obtain than it is for  $Z$ . Semi-empirical expressions for the radial distribution function of the hard sphere fluid are available (e.g., [7]), whose derivative with respect to separation at contact could be taken. An application of scaled particle theory to calculate the first and second derivatives of  $g(r)$  at contact is reported in [8]. The approach adopted here is to base  $y_1$  on integral equation solutions which are accurate at low density. For example, the Percus–Yevick, PY, solution for  $y_1$  is [9]

$$y_1^{\text{PY}}(\zeta) = -\frac{9}{2} \frac{\zeta(1 + \zeta)}{(1 - \zeta)^3}, \quad (5)$$

which we call  $y_1^{\text{PY}}$ . There are also semi-empirical modifications of the PY solution, for example, from Tao *et al* [9, 10],

$$y_1^{\text{TSM}}(\zeta) = -\frac{9}{2} \frac{\zeta(1 + \zeta)}{(1 - \zeta)^4}. \quad (6)$$

Note the difference in the exponent of the denominator between (5) and (6). Another approximation for  $y_1$  was given by del Rio and Benavides [11],

$$y_1^{\text{RB}} = y_1^{\text{PY}} \left( 1 + \frac{\zeta}{4} + \zeta^2 + 4\zeta^3 \right). \quad (7)$$

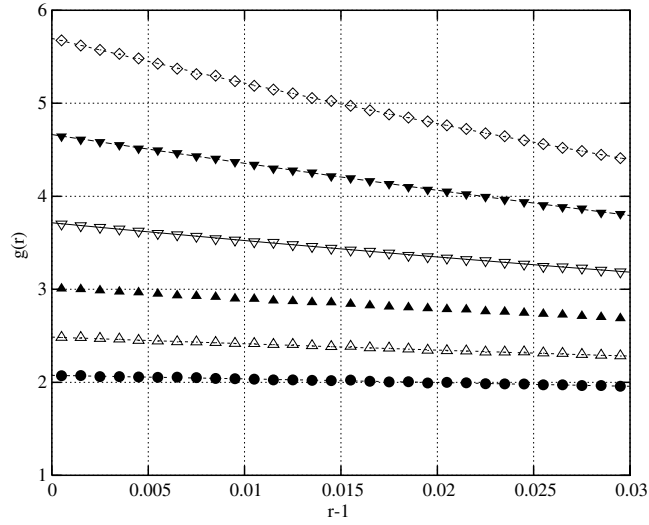
It is convenient to define the quantity

$$C(\zeta) = -y_1(\zeta)/g(\sigma, \zeta) = -\sigma d(\ln(g(r)))/dr|_{r=\sigma}, \quad (8)$$

as in each of the above cases it is more slowly varying with  $\zeta$  than  $y_1$ . Adopting the Carnahan–Starling expression for the radial distribution function at contact of the spheres, the  $C$  function in these approximations (with the superscripts of  $y_1$  now taken as subscripts)

$$C_{\text{PY}}(\zeta) = 9\zeta \frac{(1 + \zeta)}{(2 - \zeta)}, \quad (9)$$

$$C_{\text{TSM}}(\zeta) = 9\zeta \frac{(1 + \zeta)}{(2 - \zeta)} \frac{1}{(1 - \zeta)}, \quad (10)$$



**Figure 1.** The radial distribution function,  $g(r)$ , computed by MD simulation with  $N = 4000$  particles for a set of packing fractions. The curves are second order polynomial fits to the simulation points. Key: from bottom to top  $\zeta = 0.250, 0.300, 0.350, 0.400, 0.450$  and  $0.490$ .

and

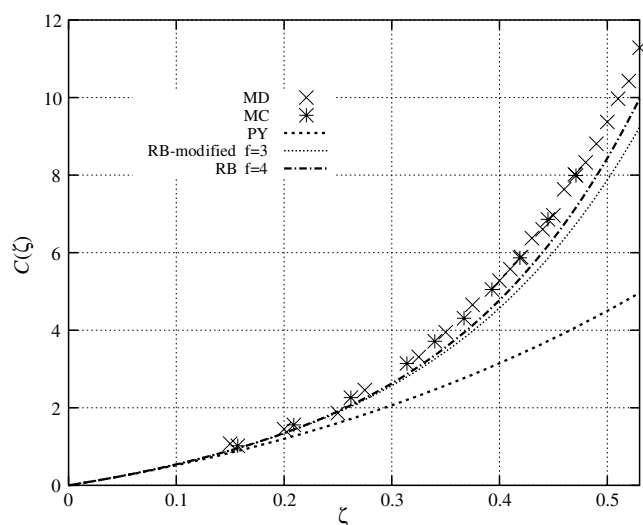
$$C_{\text{RB}}(\zeta) = 9\zeta \frac{(1 + \zeta)}{(2 - \zeta)} (1 + \zeta/4 + \zeta^2 + f\zeta^3). \quad (11)$$

where  $f = 4$ . We have also computed a variant of (11) using instead  $f = 3$ .

Molecular dynamics (MD) and Monte Carlo (MC) computer simulations are the nearest to an exact realization of the hard sphere system we can achieve. The purpose of this work is to compare the above analytic predictions for  $C(\zeta)$  with the same function computed directly by MD. The results of previous MC simulation studies of  $y_1$  [12–14] are also used in our analysis. Systems consisting of a variable number ( $N$ ) of hard spheres in the simulation cell were considered, with  $N$  in the range 192–10 976.

Simulations were carried out typically for 50–100 million hard sphere collisions, with packing fractions in the range  $\zeta = 0.05$ – $0.53$  (the fluid freezing value for hard spheres is  $0.494$  [15]), so a number of the higher density states simulated were in the metastable branch of the phase diagram. Some representative radial distribution functions of the hard sphere fluid for  $N = 4000$  systems at various packing fractions are given in figure 1. Figure 1 shows MD generated  $g(r)$  between  $r = 1.0$  and  $1.03$  in hard sphere distance units (i.e.  $\sigma \equiv 1$ ) for  $\zeta$  values between  $0.25$  and  $0.49$ . As can be seen, the value of  $g_0$  and the first derivative of  $g(r)$  at contact increase with packing fraction, in the latter case revealed by the more ‘cusp’-like appearance of  $g(r)$  as  $r \rightarrow \sigma$ .

The contact derivative of  $g(r)$  or  $y_1$  can be evaluated by fitting  $g(r)$  in the vicinity of the contact separation, i.e. for  $r \leq \sigma + x_c$ , to an expression which can then be differentiated. The fitting of  $g(r)$  is not a trivial matter as both the range of the fit,  $x_c$ , and the functional form chosen to represent  $g(r)$  can affect the value of  $y_1$ , and both must be chosen with care. A polynomial analytic form was chosen taking a low order polynomial and a suitable value of  $x_c$ . Trial and error led to the adoption of a non-linear least square fit to the formula,  $g(r) = g_0 + ax + bx^2$ , where  $x = r - \sigma$  [17], with  $x_c = 0.03\sigma$ . This was found to be a good compromise, as smaller values of  $x_c$  led to greater statistical fluctuations in the values



**Figure 2.** A plot of  $C(\zeta)$  against  $\zeta$ . ‘MD’ are the MD values (using a second order polynomial in  $r$  and  $x_c = 0.03$ ) in the thermodynamic limit. ‘MC’ are the averaged Monte Carlo values from [12, 13]. PY is the Percus–Yevick solution from equation (9). The del Rio and Benavides formula from [11] given in equation (11) is denoted as ‘RB  $f = 4$ ’, and a modification of this formula with ‘ $f = 3$ ’ is also shown.

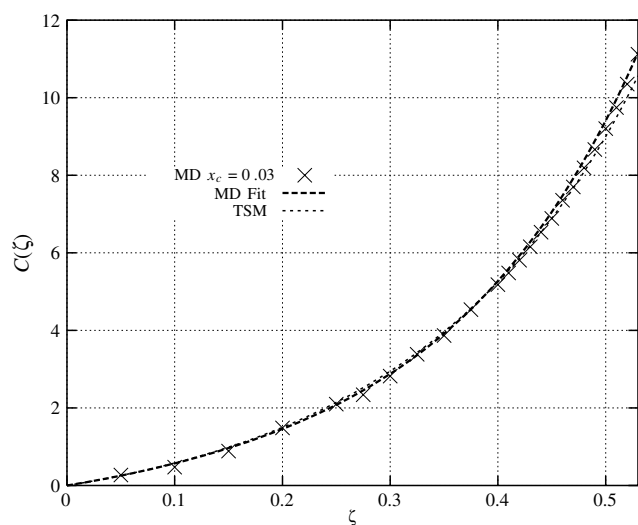
of  $y_1$  without apparent change in its value. Larger values of  $x_c$  tended to underestimate the value of  $y_1$  (this being a sign that for  $x_c > 0.03$  the second order polynomial is not a suitable functional form). At each packing fraction,  $g(\sigma)$  and the first derivative,  $g'(\sigma)$ , were obtained. These data were individually extrapolated with  $N^{-1}$  (found appropriate for thermodynamic properties [16]) to infinite  $N$  by least squares fit, and the MD derived  $C$  values quoted herein are for these values in the estimated thermodynamic limit. The  $g(\sigma)$  were obtained from the fit to the radial distribution function, and also from the average  $Z$  value from the MD simulation by the virial and collision rate routes [15], and then using  $g_0 = (Z - 1)/4\zeta$ . In the thermodynamic limit there was no statistically significant difference between these values and those derived from the Kolafa equation of state, and therefore the main source of statistical uncertainty in  $C$  was in the value of  $y_1$ .

Figure 2 shows the MD  $C(\zeta)$  in the thermodynamic limit of this work. These values fall on the same smooth curve (within the mutual simulation statistics) as the literature Monte Carlo derived values [12, 13], and these data represent therefore a precise and accurate representation of the density dependence of  $C$ . The Percus–Yevick (PY) function of equation (9) agrees well with the simulation data below about 0.15 but increasingly underestimates the simulation data for higher packing fractions. Also,  $C_{RB}$  is noticeably below the MD curve, and the variant with  $f = 3$  in equation (11) is in worse agreement.

In the spirit of  $C_{RB}(\zeta)$ , the  $C(\zeta)$  values from the MD and previous MC treatments were fitted to the function

$$C_{MD} = 9\zeta \frac{(1 + \zeta)}{(2 - \zeta)} (1 + c_1\zeta + c_2\zeta^2 + c_3\zeta^3), \quad (12)$$

by the least squares method, which gave 0.979 91,  $-0.817 47$  and 6.442 03 for  $c_1$ ,  $c_2$  and  $c_3$ , respectively. In figure 3, the formula in equation (12) is compared with the function proposed by Tao *et al* [9], which is defined in equation (10) and denoted by  $C_{TSM}$ . This function, it can be seen, follows the MD-derived curves, essentially exactly for about  $\zeta < 0.45$ , with



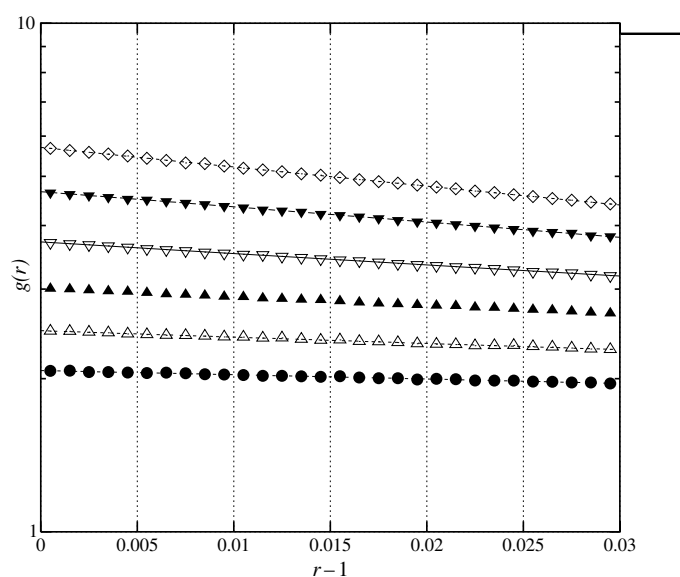
**Figure 3.** A plot of  $C(\zeta)$  against  $\zeta$ . The ‘MD Fit’ curve is from equation (12). ‘TSM’ is the formula of Tao *et al* [9] given in equation (10). The MD data points are using  $g(r) = g_0 \exp(Ax)$  with  $x_c = 0.03$ .

larger departures from the simulation data with increasing packing fraction. The symbols in this figure represent  $C$  obtained using the fit function,  $g(r) = g_0 \exp(Ax)$ , again fitted in the range  $0 \leq x \leq x_c$  for  $x_c$  equal to 0.03. For this formula,  $C = -A$ , and because there is essentially only one free parameter to fit (apart from  $g_0$ ), rather than two in the case of the second order polynomial, the statistical variation in  $C$  is much less. The statistical uncertainty is more noticeable for lower packing fractions. The exponential function representation of the radial distribution function is very good near contact, as can be seen in figure 4. This figure shows the same MD-generated radial distribution functions and intervals as in figure 1, except that they are plotted on a logarithmic scale. The linear regression fits (corresponding to the exponential representation of  $g(r)$ ) are an excellent fit to the MD data for most of the separation range shown.

To conclude, using molecular dynamics simulation data a simple formula (equation (12)) has been obtained for the normalized contact derivative of the radial distribution function,  $C$ , in the thermodynamic limit as a function of packing fraction. This applies in the whole of the fluid range and part way into the metastable region (up to  $\zeta = 0.53$ ). In the fitting procedure it is most satisfactory to use a low order polynomial and minimize the fitting range, the practicable value of the latter depending on the accuracy of the radial distribution function provided by the simulation. The expression proposed by Tao *et al* [9] is in very good agreement with this function up to a packing fraction of about 0.45. Close to contact, the radial distribution function can be represented well by a low order polynomial or an exponential function (see figure 4).

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**Figure 4.** The radial distribution function,  $g(r)$ , computed by MD simulation with  $N = 4000$  particles for a set of packing fractions and plotted on a logarithmic scale (symbols). The linear regression lines are shown. Key: from bottom to top  $\zeta = 0.25, 0.30, 0.35, 0.40, 0.45$  and  $0.49$ .

collaboration. The work has been partially supported by the Polish Ministry of Education and Science.

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