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# The structure factor and equation of state of hard-sphere fluids

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## Abstract

In a paper by Verberg *et al* (2002 *Dynamics: Models and Kinetic Methods for Non-Equilibrium Many Body Systems* ed J Karkheck (Dordrecht: Kluwer)) it was shown that the static structure factor  $S(k)$  of a hard-sphere fluid plays an important role in the computation of the transport properties of colloidal suspensions. To perform actual calculations, those authors used a semiempirical form due to Grundke and Henderson which stems out of the Percus–Yevick approximation. In this work we present calculations of the static structure factor of a hard-sphere fluid within the rational function approximation method (Bravo Yuste *et al* 1996 *Phys. Rev. E* **53** 4820) which is wholly compatible with the equation of state used for the fluid. The Carnahan–Starling equation of state (Carnahan and Starling 1969 *J. Chem. Phys.* **51** 635), the Padé (4, 3) of van Rensburg (1993 *J. Phys. A: Math. Gen.* **26** 4805) and Sánchez (1994 *J. Chem. Phys.* **101** 7003), the equation of state of Malijevský and Veverka (1999 *Phys. Chem. Chem. Phys.* **1** 4267) and a recent proposal by us (Robles and López de Haro 2003 *Europhys. Lett.* **62** 56) will be explicitly examined.

## 1. Introduction

The two basic quantities employed to study the structure of a fluid in equilibrium are the radial distribution function (RDF)  $g(r)$  and its close relative the (static) structure factor  $S(k) = 1 + \rho \int \mathbf{dr} e^{-i\mathbf{k}\cdot\mathbf{r}} [g(r) - 1]$ , where  $\rho$  is the density. The importance of  $g(r)$  and  $S(k)$  is also due to the fact that, given the interparticle potential, their knowledge as functions of density and temperature allows one to derive the equation of state using either of the two well established statistical mechanical virial or compressibility routes [8]. Furthermore, these equilibrium structural quantities also appear in theoretical formulae of transport coefficients, for instance those of the Enskog kinetic theory [9] or of colloidal suspensions [1].

The commonest approaches to determine  $g(r)$  are through the use of one of the integral equation theories of liquids or through computer simulation. And it is only in the case of

hard spheres and in the so-called Percus–Yevick (PY) approximation that an exact analytical solution has been found [10, 11]. In general, integral equation theories require hard numerical work as well as closure approximations, and they lead to different equations of state if one takes the virial or the compressibility routes (thermodynamic inconsistency problem). As a matter of fact, the PY solution for the hard-sphere fluid also presents this problem, and so Verlet and Weis [12] added an empirical correction term to the PY  $g(r)$  in which the parameters were adjusted so that the resulting equation of state taking either of the two thermodynamic routes coincides with the expression proposed by Carnahan and Starling (CS) [3]. The  $S(k)$  that follows from the Verlet and Weis proposal was obtained by Grundke and Henderson (GH) [13].

A few years ago, an alternative (algebraic) approach [2, 16, 17] to the integral equation theories of liquids was introduced to obtain the structural properties of hard-sphere fluids and their mixtures. Apart from its relative simplicity, this approach—referred to as the rational function approximation (RFA) method—completely avoids the thermodynamic inconsistency problem, in that the compressibility factor is involved in the derivation of both  $g(r)$  and  $S(k)$ , and the results are then thermodynamically compatible by construction. The major aim of the present work is to assess the effect of considering different equations of state proposed in the literature for a hard-sphere fluid on the actual values of the static structure factor as a function of the density computed using the RFA approach.

The presentation is organized as follows. In order to make it self-contained, in the next section we provide a brief outline of the derivation of the analytical formulae for  $g(r)$  and  $S(k)$  in the RFA method. This is followed by the actual results for the static structure factor as a function of density using four different equations of state, and a comparison of the corresponding results with those obtained with the GH expression. We close this work with some further discussion and concluding remarks.

### 1.1. The RFA method

In the PY approximation, Wertheim [10] has shown that for a hard-sphere (HS) fluid the Laplace transform of  $\frac{r}{\sigma}g_{\text{HS}}(\frac{r}{\sigma})$  has an exact solution of the form

$$G(t) = \mathcal{L}\left[\frac{r}{\sigma}g_{\text{HS}}\left(\frac{r}{\sigma}\right)\right] = \frac{t}{12\eta} \frac{1}{1 - e^t \Phi(t)}, \quad (1)$$

where  $\eta = \frac{\pi}{6}\rho\sigma^3$  is the packing fraction of the spheres ( $\rho$  is the number density and  $\sigma$  the hard-sphere diameter) and  $\Phi(t)$  is a rational function given by

$$\Phi_{\text{PY}}(t) = \frac{1 + S_1^{\text{PY}}t + S_2^{\text{PY}}t^2 + S_3^{\text{PY}}t^3}{1 + L_1^{\text{PY}}t}, \quad (2)$$

where the coefficients  $S_1^{\text{PY}}$ ,  $S_2^{\text{PY}}$ ,  $S_3^{\text{PY}}$  and  $L_1^{\text{PY}}$  are well known analytical functions of the packing fraction  $\eta$ , and the label PY denotes the PY results.

The RFA method [2, 16] is based on the assumption that a reasonable extension of the Wertheim solution beyond the PY approximation consists of adopting the form depicted in equation (1) but taking

$$\Phi(t) = \frac{1 + S_1t + S_2t^2 + S_3t^3 + S_4t^4}{1 + L_1t + L_2t^2} \quad (3)$$

where the (so far unknown) six coefficients  $S_1$ ,  $S_2$ ,  $S_3$ ,  $S_4$ ,  $L_1$  and  $L_2$  may be evaluated in an algebraic form by imposing the following two requirements [18].

- (i) The first integral moment of the total correlation function  $h_{\text{HS}}(r) \equiv g_{\text{HS}}(r) - 1$ , i.e.  $\int_0^\infty r h_{\text{HS}}(r) dr$ , must be well defined and non-zero.

- (ii) The compressibility factor  $Z_{HS} = P/\rho k_B T \equiv 1 + 4\eta g_{HS}(\sigma^+)$  (where  $P$  is the pressure,  $k_B$  the Boltzmann constant and  $T$  the temperature) must be compatible with the isothermal susceptibility and the radial distribution function, in the sense that on the one hand  $\chi_{HS} = (d(\rho Z_{HS})/d\rho)^{-1}$  and simultaneously  $\chi_{HS} = 24\eta(1 + \int_0^\infty r^2 h_{HS}(r) dr)$ .

Using the first requirement one finds that

$$L_1 = \frac{1}{2} \frac{\eta + 12\eta L_2 + 2 - 24\eta S_4}{2\eta + 1}, \tag{4}$$

$$S_1 = \frac{3}{2} \eta \frac{-1 + 4L_2 - 8S_4}{2\eta + 1}, \tag{5}$$

$$S_2 = -\frac{1}{2} \frac{-\eta + 8\eta L_2 + 1 - 2L_2 - 24\eta S_4}{2\eta + 1}, \tag{6}$$

$$S_3 = \frac{1}{12} \frac{2\eta - \eta^2 + 12\eta^2 L_2 - 12\eta L_2 - 1 - 72\eta^2 S_4}{(2\eta + 1)\eta}, \tag{7}$$

and with the second one

$$L_2 = -3(Z_{HS} - 1)S_4, \tag{8}$$

$$S_4 = \frac{1 - \eta}{36\eta(Z_{HS} - 1/3)} \left[ 1 - \left[ 1 + \frac{Z_{HS} - 1/3}{Z_{HS} - Z_{PY}} \left( \frac{\chi}{\chi_{PY}} - 1 \right) \right]^{1/2} \right]. \tag{9}$$

Here,  $Z_{PY} = \frac{1+2\eta+3\eta^2}{(1-\eta)^2}$  and  $\chi_{PY} = \frac{(1-\eta)^4}{(1+2\eta)^2}$  are the compressibility factor and isothermal susceptibility arising in the PY theory. To close the problem one has to give an expression for  $Z_{HS}$ , so all the procedure is a function of this choice. For a given  $Z_{HS}$  the radial distribution function is then given by

$$g_{HS} \left( \frac{r}{\sigma} \right) = \frac{\sigma}{12\eta r} \sum_{n=1}^\infty \varphi_n \left( \frac{r}{\sigma} - n \right) \theta \left( \frac{r}{\sigma} - n \right), \tag{10}$$

with  $\theta(\frac{r}{\sigma} - n)$  the Heaviside step function and

$$\varphi_n \left( \frac{r}{\sigma} \right) = \mathcal{L}^{-1} \left[ -t [\Phi(t)]^{-n} \right]. \tag{11}$$

Explicitly, using the residues theorem,

$$\varphi_n(x) = - \sum_{n=1}^4 e^{t_i x} \sum_{m=1}^n \frac{A_{mn}(t_i)}{(n-m)!} x^{n-m}, \tag{12}$$

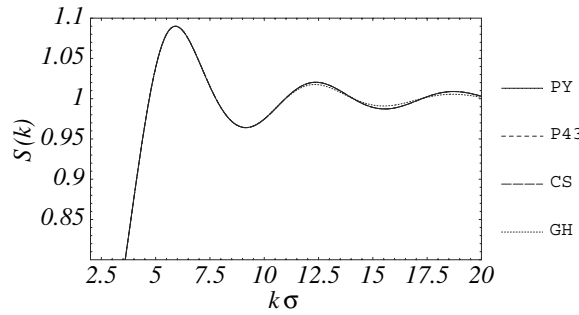
where

$$A_{mn}(t_i) = \lim_{t \rightarrow t_i} \frac{1}{(m-1)!} \left( \frac{d}{dt} \right)^{m-1} (t - t_i) t [\Phi(t)]^{-n}, \tag{13}$$

$t_i$  being the roots of  $1 + S_1 t + S_2 t^2 + S_3 t^3 + S_4 t^4 = 0$ . On the other hand, the static structure factor  $S(k)$  is related to  $G(t)$ , (which also explicitly depends on  $Z_{HS}$ , cf equations (1), (3)–(9)), by

$$S(k) = 1 - 24\eta \operatorname{Re} \left. \frac{t^2 G(t) - 1}{t^3} \right|_{t=ik}. \tag{14}$$

Therefore, the only required input to compute the structure factor within this method is  $Z_{HS}$ . In the next section we consider various choices for the hard-sphere compressibility factor to illustrate the effect of considering different equations of state on the actual values of the structure factor.



**Figure 1.** The structure factor computed with the RFA method using the equations of state cited in the text at  $\eta = 0.1$ . The curves labelled GH and PY are the results of using the Grundke and Henderson and Percus–Yevick approximations, respectively.

## 2. The static structure factor $S(k)$

In order to proceed with the calculations we need an explicit expression for  $Z_{\text{HS}}$ . A very popular and relatively accurate equation of state for the hard-sphere fluid is the one due to Carnahan and Starling [3] which yields

$$Z_{\text{HS}}^{\text{CS}} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (15)$$

Other proposals in the literature include the Padé (4, 3) of van Rensburg [4] and Sánchez [5] (which reproduces the known eight virial coefficients and has a pole at the close-packing fraction  $\eta_{\text{cp}} = 0.7405$ )

$$Z_{\text{HS}}^{(4,3)} = \frac{1 + 1.0244\eta + 1.1045\eta^2 - 0.4611\eta^3 - 0.7430\eta^4}{1 - 2.9756\eta + 3.0070\eta^2 - 1.0978\eta^3}, \quad (16)$$

the presumably most accurate up to now (with respect to simulation data) equation of state of Malijevský and Veverka [6]

$$Z_{\text{HS}}^{\text{MV}} = \frac{1 + 1.0560\eta + 1.6539\eta^2 + 0.3262\eta^3}{(1 + 0.0560\eta + 0.5979\eta^2 + 0.3076\eta^3)(1 - \eta)^3} \quad (17)$$

and our own recent *ad hoc* proposal [7], which was built to reproduce the first eight virial coefficients arising from the Carnahan–Starling equation of state and to have a pole at the random close-packing fraction. It reads

$$Z_{\text{HS}}^{\text{LHR}} = \frac{1 + 0.1535\eta - 0.4284\eta^2 - 2.7981\eta^3 - 0.31742\eta^4 - 0.1058\eta^5}{1 - 3.8464\eta + 4.9574\eta^2 - 2.1639\eta^3}. \quad (18)$$

By substituting the various former expressions for  $Z_{\text{HS}}$  in equations (4)–(9) and making use of the resulting coefficients in equation (3), one obtains corresponding results for  $G(t)$  from equation (1) and subsequently for  $S(k)$  from equation (14). It should be pointed out that while  $Z_{\text{HS}}^{\text{CS}}$  and  $Z_{\text{HS}}^{\text{MV}}$  lead to physically meaningful structural properties for  $0 \leq \eta \leq 1$ , in the case of  $Z_{\text{HS}}^{(4,3)}$  the method leads to a threshold packing fraction [2] (identified with the packing fraction at which a glass transition in the hard-sphere fluid takes place)  $\eta_0^{(4,3)} = 0.5604$  beyond which no meaningful fluid structure can be derived. The same applies to  $Z_{\text{HS}}^{\text{LHR}}$ , but in this instance the threshold packing fraction is  $\eta_0^{\text{LHR}} = 0.5684$ .

In figures 1–4 we present the results for  $S(k)$  at a fixed packing fraction for the four different compressibility factors and their comparison with those derived using the GH expression [13]

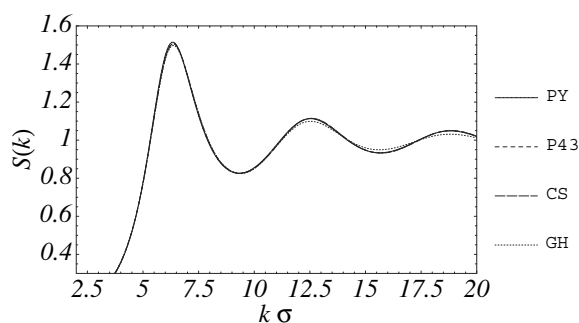


Figure 2. The same as figure 1 for  $\eta = 0.3$ .

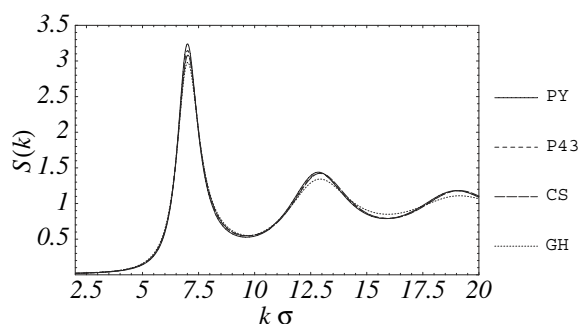
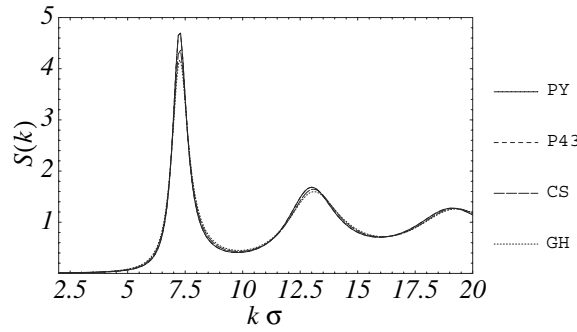


Figure 3. The same as figure 1 for  $\eta = 0.5$ .

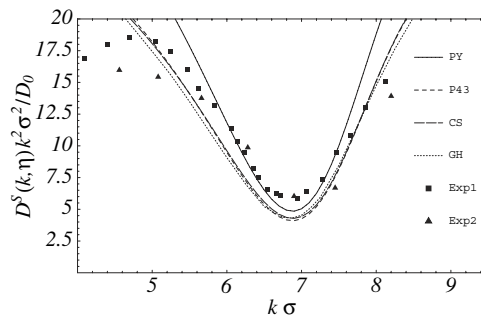
and the PY theory. The curves corresponding to equations (17) and (18) are practically indistinguishable from those obtained from the CS equation, and they have been omitted in all figures to avoid overcrowding. While at the lowest packing fraction of  $\eta = 0.1$  there is virtually no difference in the results, irrespective of the choice for  $Z_{\text{HS}}$  or the use of the GH formula, as  $\eta$  increases differences both in the positions and heights of the peaks become manifest, and they are more important for the highest packing fraction of  $\eta = 0.56$ . Note that both in figures 3 and 4 the height of the first peak exceeds 2.85 which, according to an empirical criterion [14], indicates that we have gone beyond the fluid–solid transition and into the metastable fluid regime. As discussed in [7], a comparison between the contact values of the RDF stemming out of the different compressibility factors considered here and those obtained through simulation [15] within this metastable regime shows very good agreement. Also notice that, in the case of figure 4, the value taken for  $\eta$  is close to the one of  $\eta_0$  if  $Z_{\text{HS}}^{\text{LHR}}$  or  $Z_{\text{HS}}^{(4,3)}$  are considered. Whether an empirical criterion to locate the glass transition based on the value of the first peak of  $S(k)$  at such a packing fraction can be established, similar to the one used for the fluid–solid transition, is worth investigating.

### 3. Concluding remarks

To our knowledge, there are no computer simulation results for the static structure factor of a hard-sphere fluid in the metastable fluid regime. Therefore an assessment of the merits and limitations of taking one or other compressibility factor on the basis of a comparison with simulation data is precluded at this stage. Nevertheless, we will attempt to put some



**Figure 4.** The same as figure 1 for  $\eta = 0.56$ . Note that, although not appreciated in the scale of this figure, the GH approximation is (incorrectly) negative for small values of  $k\sigma$  at this packing fraction.



**Figure 5.** The reduced short-time collective diffusion coefficient as a function of  $k\sigma$  for  $\eta = 0.443$ . The curves represent the RFA solutions for the aforementioned HS equations of state. The PY and GH approximations are also included for comparison. The experimental data (exp1 and exp2) were taken from [19] and [20], respectively.

perspective on the previous results by examining their performance in connection with the diffusion coefficient of a colloidal dispersion. According to the theory of Verberg *et al* [1], the short-time collective diffusion coefficient of a concentrated colloidal suspension  $D^S(k, \eta)$  may be expressed as

$$D^S(k, \eta) = \frac{D_0 d(k)}{g_{\text{HS}}(\sigma^+; \eta) S(k; \eta)}, \quad (19)$$

where  $D_0$  is the Stokes–Einstein diffusion coefficient of an isolated Brownian particle,  $d(k) = [1 - j_0(k\sigma) + 2j_2(k\sigma)]^{-1}$  with  $j_l(k\sigma)$  the spherical Bessel function of order  $l$  and the notation  $g_{\text{HS}}(\sigma^+; \eta)$  and  $S(k; \eta)$  indicates that the contact value  $g_{\text{HS}}(\sigma^+)$  and the static structure factor  $S(k)$  depend on the packing fraction  $\eta$ . In figure 5 we display the experimental measurements [19, 20] related to this coefficient in suspensions of neutral PMMA spheres stabilized with poly-(12-hydroxystearic acid) at a packing fraction of  $\eta = 0.494$  together with the predictions using the structure factors that follow from each  $Z_{\text{HS}}$ . The experiments, geared to determine the  $k$ -dependent diffusion coefficient from the dynamic structure factor, involve the two-colour dynamic light scattering method; interestingly enough, in [19] they were able to observe a glass transition at a packing fraction  $\eta \simeq 0.56$ . One notices that the effect of using any  $Z_{\text{HS}}$  instead of the GH formula and the CS equation of state as done in the original theoretical calculations [1] is hardly noticeable, except for the PY curve. To compute this

curve we used the contact values  $g_{HS}(\sigma^+; \eta)$  that follow from the virial route, and it is due to such values that the ‘apparent’ improvement is achieved. Nevertheless, it is well known that the PY compressibility factor underestimates the true value, and so the better agreement with the experimental data in this instance is fortuitous.

In summary, in this work we have provided an analysis of the effect of using different compressibility factors within the RFA method to compute the static structure factor of a hard-sphere fluid. Clearly, being an integral moment, this effect is not very noticeable except at high densities, and even there only minor differences show up. We were not able to perform a comparison with computer simulation data but, in order to see whether these minor differences could manifest themselves in a different context, an indirect comparison through the short-time collective diffusion coefficient of a concentrated suspension of PMMA spheres was performed. This comparison confirmed that the effect of using different compressibility factors is negligible, and thus the discrepancy between theory and experiment cannot be ascribed to a lack of accuracy in the equation of state used. Indirectly, therefore, our results give support to the validity of the theory by Verberg *et al* [1] for the transport properties of concentrated colloidal suspensions.

Finally, it is worth pointing out that the availability of analytical expressions for the static structure factor, as derived with the use of the RFA method, could perhaps be profitably exploited in connection with mode coupling theory [21] to predict the glass transition in colloidal systems. We plan to conduct efforts along this direction in the near future.

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