

Correlation functions I: formalism and simple applications

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ABSTRACT. The aim of this work, first of a series of papers with a pedagogical character, is to discuss the background in the formalism developed on the basis of the Wertheim-Baxter method. This method was applied for the uncoupling of the correlation functions that appear in the Ornstein-Zernike (OZ) equation. We present the well known results for hard spheres (HS) and sticky hard spheres (SHS) systems with detail and discuss the sticky potential interpretation.

RESUMEN. El objeto de este trabajo, primero de una serie de carácter pedagógico, es discutir los fundamentos del formalismo desarrollado sobre la base del método de Baxter-Wertheim. Este método fue aplicado en el desacoplamiento de las funciones de correlación que aparecen en la ecuación de Ornstein-Zernike (OZ). Presentamos los bien conocidos resultados para los sistemas de esferas duras y esferas duras adherentes con detalle y discutimos la interpretación del potencial adherente.

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1. INTRODUCTION

The aim of the theory of liquids is to understand why particular phases of fluids are stable in a particular range of temperatures and densities and to relate this behavior with the characteristic magnitudes of their components (molecules, atoms or ions).

A great deal of research on the theory of liquids and dense systems has been based on the original works of Baxter and Wertheim [1,2], in which they have developed a method based on the factorization of the Ornstein-Zernike (OZ) equation [3] using the Wiener-Hopf [4] technique, which gives, in a natural way, auxiliary functions called factor correlation functions (FCF).

The OZ equation is a convolution integral equation that involves the direct ($c(r)$) and total ($h(r)$) correlation functions as

$$h(r) - c(r) = \rho \int ds h(s)c(|r - s|). \quad (1)$$

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The use of approximate relationships between the direct $c(r)$ and total $h(r)$ correlation functions give us a possibility of the closed solution of the OZ equation. These relationships have been proposed in different ways, namely, Percus-Yevick (PY), mean spherical (MSA), hypernetted-chain (HNC), and other approximations [5].

In this work (first of a series of papers) a review is made of the Baxter's factor correlation functions (FCF) applied to different fluid systems: hard spheres (HS) and sticky hard spheres (SHS) in the PY approximation. The discussion involves the explicit derivation of these functions and the thermodynamic properties of both systems associated with the FCF's.

The factor correlation functions for other systems (such as electrolytes, dipoles and dipole mixtures) will be discussed in future works.

The study of liquid systems requires to take into account that the interactions between the particles are basically electromagnetic and that the qualitative and quantitative predictions of the properties of fluids would be found with the solution of the many-body Schrödinger equation that involves all the nuclei and electrons of the system [5].

There exist some important simplifications that allow us to avoid this exceedingly difficult task. The first one consists in the derivation of the potential energy depending only on the nuclei coordinates due to the fact that the nuclei masses are much greater than the electron mass and to the assumption of symmetrical molecules, *i.e.*, the potential energy does not depend on their orientation [5]. As a consequence of the high mass ratio the system can be described by classical mechanics or classical statistical mechanics. At first approximation, the inter molecular potential energies can be taken as pairwise additive:

$$U_N = \sum_{i < j} u(r_{ij}) = \sum_{i < j} u(|\mathbf{r}_i - \mathbf{r}_j|), \quad (2)$$

where \mathbf{r}_i and \mathbf{r}_j are the position vectors of particles i and j .

The triplet and higher order terms in the expansion of the potential energy can be accounted for by using perturbative techniques.

With the above simplifications, the probability of finding L particles with coordinates in $(d\mathbf{r}_1, \dots, d\mathbf{r}_L)$ and momenta in $(d\mathbf{p}_1, \dots, d\mathbf{p}_L)$, is given by

$$\mathcal{P} \prod_{i=1}^N d\mathbf{r}_i d\mathbf{p}_i, \quad (3)$$

with

$$\mathcal{P} = \frac{1}{h^{3N} \Theta} e^{\beta(N\mu - E)}, \quad (4)$$

where μ is the chemical potential, $\beta = 1/kT$, where k is Boltzmann's constant and T the absolute temperature, h is Planck's constant and N the total number of particles in the system.

The differential factors in Eq. (3) represent three-dimensional elements of volume and momenta for each particle— i , i.e., $d\mathbf{r}_i d\mathbf{p}_i$ is a six-dimensional volume element of phase space for the particle i , and E , given the initial simplifications can be written as

$$E = \sum_{i=1}^N \frac{\mathbf{p}_i^2}{2m_i} + \sum_{i<j}^N u_{ij}(r). \quad (5)$$

The normalization factor $\Theta = \Theta(\mu, V, T)$ is the grand partition function

$$\Theta = \sum_{N=1}^{\infty} \frac{e^{\beta N \mu}}{h^{3N} N!} \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_N d\mathbf{p}_1 \cdots d\mathbf{p}_N e^{-\beta E}. \quad (6)$$

If we define the configuration integral as

$$\mathcal{Z}_N = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U_N}, \quad (7)$$

Equation (6) can be written as

$$\Theta = \sum_{N=1}^{\infty} \frac{z^N}{N!} \mathcal{Z}_N,$$

where the result of integration over momenta has been introduced in the fugacity z . Since $\mu = kT \ln(z)$, then the difference in chemical potentials between two states is given by $\Delta\mu = kT \ln(a_2/a_1)$, where a_1 and a_2 are the activities (see Ref. [6]).

Given an explicit interaction potential it is possible, at least formally, to obtain the thermodynamics of a system, by means of the previous equations written for the grand canonical ensemble. In the case of liquid systems, however, it is more convenient to use the language of distribution functions. These will be introduced, with the discussion of a hard-sphere system, in the following section [6,7].

2. HARD-SPHERE SYSTEM. THE CORRELATION FUNCTIONS

Consider a system formed by mixed species of hard spheres (different diameters). A convenient treatment of mixtures of neutral hard spheres is provided by the Percus-Yevick (PY) theory [8]. The simplest possible model of a fluid is a system of hard spheres, for which the pair potential $u_{ij}(r)$ is given by

$$u_{ij} = u_{ij}(r) = \begin{cases} 0, & \text{if } r = |\mathbf{r}_i - \mathbf{r}_j| > R_{ij}, \\ \infty, & \text{if } r < R_{ij}, \end{cases} \quad (8)$$

where $R_{ij} \equiv (R_i + R_j)/2$ assumes additive diameters. This simple model is ideally suited for the study of phenomena in which the hard core of the potential is the dominant factor [9].

The probability of finding a particle i at \mathbf{r} can be computed using the Dirac delta function

$$\delta(\mathbf{r}_i - \mathbf{r}) = \frac{1}{8\pi^3} \int d\mathbf{k} e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r})}, \quad (9)$$

and is given by

$$\begin{aligned} \rho_i(\mathbf{r}) &= \sum_{j=1}^{N_i} \langle \delta(\mathbf{r}_j - \mathbf{r}) \rangle = \frac{1}{\mathcal{Z}_N} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U_N} \sum_{j=1}^{N_i} \delta(\mathbf{r}_j - \mathbf{r}) \\ &= \left\langle \frac{N_i}{V} \right\rangle = \rho_i, \end{aligned} \quad (10)$$

where N_i is the particle number of i -species.

The combined probability of finding two particles, at \mathbf{r}_1 and \mathbf{r}_2 , respectively, is given by

$$\begin{aligned} \rho_{ij}(\mathbf{r}_1, \mathbf{r}_2) &= \sum_{i,j=1}^N \langle \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \rangle = \rho_i \rho_j g_{ij}(r_{12}) \\ &= \rho_i \rho_j g_{ij}(r), \end{aligned} \quad (11)$$

where the function $g_{ij}(r)$, called the radial distribution function, has been introduced. For the simpler case of a pure fluid, it is given by

$$\rho(r_{12}) = \frac{N(N-1)}{\mathcal{Z}_N} \int d\mathbf{r}_3 \cdots d\mathbf{r}_N e^{-\beta U_N} = \rho^2 g(r_{12}). \quad (12)$$

Using Eq. (2) we can rewrite the exponential as

$$\begin{aligned} e^{-\beta U_N} &= e^{-\beta \sum u_{ij}} = \prod_{i>j} e^{-\beta u_{ij}} = \prod_{i>j} (1 + f_{ij}) \\ &= 1 + \sum f_{ij} + \sum \sum f_{ij} f_{kl} + \cdots, \end{aligned} \quad (13)$$

where

$$f_{ij}(r) = e^{-\beta u_{ij}(r)} - 1 \quad (14)$$

is the Mayer function.

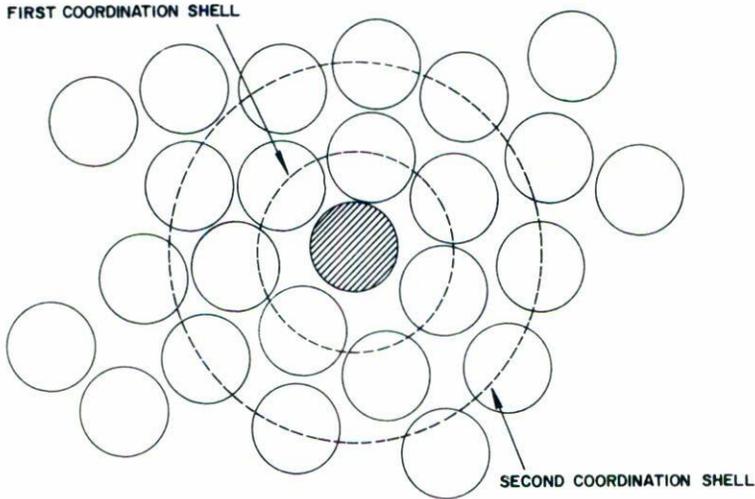


FIGURE 1. Liquid structure: schematic representation of the radial distribution function. Note that it represents the first layers around of a choice molecule and shows a short-range order.

Now, for a hard spheres interaction potential [see Eq. (8)] we have

$$e_{ij} = e^{-\beta u_{ij}(r)} = \begin{cases} 1, & r > R_{ij} \\ 0, & r \leq R_{ij}, \end{cases} \quad (15)$$

$$f_{ij} = f_{ij}(r) = e_{ij} - 1 = \begin{cases} 0, & r > r_{ij} \\ -1, & r \leq r_{ij}. \end{cases} \quad (16)$$

Without going into details, we notice the following properties of the expansion of the pair correlation function [Eqs. (11)-(12)], as given by (13):

$$g(r) = g(r_{12}) = \frac{N(N-1) \int dr_3 \cdots dr_N \prod_{i>j} (1 + f_{ij})}{\rho^2 \int dr_1 \cdots dr_N \prod_{i>j} (1 + f_{ij})}. \quad (17)$$

Note that in expression (17) the integration in the numerator is made in r_3, \dots, r_N only. A schematic view of this function, drawn in two dimensions, can be seen in Fig. 1.

The diagrammatic formulation can be reviewed in Stell, Hiroike and Chandler-Andersen-Weeks [10]. The end result is

$$g(r_{12}) = 1 + \begin{array}{c} \text{---} \\ \text{1} \quad \text{2} \end{array} + \dots$$

$$= 1 + f(r_{12}) + \left\{ \text{sum of all topologically different, connected diagrams on two white 1-circles, with no articulation.} \right\}, \quad (18)$$

where the graphs represent products of integrals of f -functions and white circles are root points, black circles are $\rho \int dr$ operators and lines are $f(r)$ factors so that

$$\begin{array}{c} \circ \text{---} \circ \\ 1 \quad 2 \end{array} \rightarrow f(r_{12}) = -\theta(R - r_{12}), \tag{19}$$

where R is the diameter of hard spheres and $\theta(x)$ is the Heaviside function:

$$\theta(x) = \begin{cases} 0, & \text{if } x < 0, \\ 1, & \text{if } x > 0, \end{cases} \tag{20}$$

and we have

$$\begin{array}{c} \bullet \\ / \quad \backslash \\ \circ \quad \circ \\ 1 \quad 2 \end{array} \rightarrow \rho \int d\mathbf{r}_3 f(r_{13})f(r_{32}) \tag{21}$$

and

$$\begin{array}{c} \bullet \text{---} \bullet \\ | \quad | \\ \circ \quad \circ \\ 1 \quad 2 \end{array} \rightarrow \rho^2 \int d\mathbf{r}_3 d\mathbf{r}_4 f(r_{13})f(r_{34})f(r_{42}). \tag{22}$$

When an articulation circle (white or black) is removed from a diagram, the diagram falls apart into at least one disconnected part with no white circles.

A function of considerable interest is the mean force potential [10,11] related to the radial distribution function by

$$g(r) = e^{-\beta w(r)}. \tag{23}$$

The formulation of approximate expressions for $w(r)$ requires another correlation function, the direct correlation function introduced originally by Ornstein-Zernike (OZ) [3]:

$$h_{ij}(r) = c_{ij}(r) + \sum_k \rho_k \int d\mathbf{r}' h_{ik}(r')c_{kj}(|\mathbf{r} - \mathbf{r}'|), \tag{24}$$

where the sum on k refers to the species in the mixture and the total correlation function is given by (an elementary discussion of the total correlation function, for a monodisperse system, can be seen in Ref. [7])

$$h_{ij}(r) = g_{ij}(r) - 1. \tag{25}$$

The OZ equation means that the total correlation between particles 1 and 2 is given by the direct correlation between them [first term of r.h.s. of (24)] and the sum of the direct or total correlations of 1 with 3 (variable) and 3 with 2 [integrals sum in the r.h.s. of (24)].

The importance of the direct correlation function is that it has a simple structure, and that simple approximations for it work very well in many cases [10]:

$$\begin{aligned}
 c(r_{12}) &= \text{○} - \text{○} + \text{○} \triangle \text{○} + \left\{ 2 \begin{array}{c} \bullet \\ | \\ \text{○} - \text{○} \\ | \\ \text{○} \end{array} + \begin{array}{c} \bullet \quad \bullet \\ | \quad | \\ \text{○} - \text{○} \\ | \quad | \\ \text{○} \end{array} + \frac{1}{2} \begin{array}{c} \bullet \\ / \quad \backslash \\ \text{○} \quad \text{○} \\ \backslash \quad / \\ \bullet \end{array} + \frac{1}{2} \begin{array}{c} \bullet \\ / \quad \backslash \\ \text{○} \quad \text{○} \\ \backslash \quad / \\ \bullet \end{array} + \dots \right\} \\
 &= \left\{ \text{sum of all diagrams of } g_{12}(r) \text{ Eq. (18) that have} \right. \\
 &\quad \left. \text{no cutting circles} \right\} \tag{26}
 \end{aligned}$$

When a cutting circle is removed from a diagram, the diagram falls apart into two (or more) disconnected pieces which may or may not contain a white circle.

On the other hand, from Eq. (23) we have

$$\beta w_{12}(r) = -\ln g_{12}(r)$$

$$\begin{aligned}
 &= \beta u_{12}(r) + \begin{array}{c} \bullet \\ / \quad \backslash \\ \text{○} \quad \text{○} \end{array} + \begin{array}{c} \bullet \quad \bullet \\ | \quad | \\ \text{○} - \text{○} \\ | \quad | \\ \text{○} \end{array} + 2 \begin{array}{c} \bullet \quad \bullet \\ | \quad | \\ \text{○} - \text{○} \\ | \quad | \\ \text{○} \end{array} + \frac{1}{2} \begin{array}{c} \bullet \\ / \quad \backslash \\ \text{○} \quad \text{○} \\ \backslash \quad / \\ \bullet \end{array} + \begin{array}{c} \bullet \\ / \quad \backslash \\ \text{○} \quad \text{○} \\ \backslash \quad / \\ \bullet \end{array} + \dots \tag{27}
 \end{aligned}$$

Comparing the diagrams of $h_{12}(r)$, $c_{12}(r)$ and $w_{12}(r)$ we can see that

$$\ln g_{12}(r) = -\beta u_{12}(r) + h_{12}(r) - c_{12}(r) + \frac{1}{2} \begin{array}{c} \bullet \\ / \quad \backslash \\ \text{○} \quad \text{○} \\ \backslash \quad / \\ \bullet \end{array} + \left\{ \begin{array}{l} \text{higher} \\ \text{order} \\ \text{bridge} \\ \text{diagrams} \end{array} \right\}$$

or, rewriting,

$$c_{12}(r) = -\beta u_{12}(r) + h_{12}(r) - \ln g_{12}(r) + \{\text{bridge diagrams}\}. \tag{28}$$

Here we call {bridge diagrams} the sum of the higher order diagrams in the expansion.

The different approximations made for $c(r)$ allow us to solve the Ornstein-Zernike equation for various systems. The hypernetted chain approximation (HNC) cuts all the terms corresponding to bridge diagrams from Eq. (28):

$$c(r) = -\beta u(r) + h(r) - \ln g(r) \tag{29}$$

or, expanding the logarithm and considering that $\lim_{r \rightarrow \infty} h(r) = 0$,

$$c(r) = -\beta u(r). \tag{30}$$

All the terms are of short range except the first in the right hand side of Eq. (27). This fact permits us to consider only this first term as an approximation for $c(r)$ for long range potentials. This is the mean spherical approximation (MSA).

For our system of hard spheres the MSA is equivalent to Percus-Yevick approximation (PYA) and is written as [12-14]

$$\begin{cases} c_{ij}(r) = 0, & \text{for } r > R_{ij}, \\ h_{ij}(r) = -1, & \text{for } r < R_{ij}. \end{cases} \quad (31)$$

The OZ Eq. (24) for a system of hard spheres was first solved by Wertheim and Thiele [2,15] and although there exist several ways to solve it, subject to the PY closure conditions [Eq. (31)], we choose the simplest, in our opinion, developed by Baxter [1,13].

3. FACTORIZATION OF THE ORNSTEIN-ZERNIKE EQUATION

Consider first the Fourier transforms of the OZ Eq. (24) for a pure fluid of hard spheres:

$$\begin{aligned} \tilde{c}(k) &= \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} c(r), \\ \tilde{h}(k) &= \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} h(r). \end{aligned}$$

By integrating the angular part we have

$$\tilde{c}(k) = 4\pi \int dr r^2 j_0(kr) c(r), \quad (32)$$

where

$$j_0(kr) = \frac{\sin kr}{kr}. \quad (33)$$

Integrating by parts

$$\tilde{c}(k) = 2 \int_0^R dr S(r) \cos(kr), \quad (34)$$

with

$$S(r) = 2\pi \int_r^R ds s c(s). \quad (35)$$

Similarly

$$\tilde{h}(k) = 4\pi \int_0^\infty dr r^2 j_0(kr) J(r), \quad (36)$$

with

$$J(r) = 2\pi \int_r^\infty ds s h(s). \quad (37)$$

The Fourier transform of the OZ equation is therefore

$$\tilde{h}(k) - \tilde{c}(k) = \rho \int d\mathbf{r}_{12} e^{i\mathbf{k}\cdot\mathbf{r}_{12}} \int d\mathbf{r}_3 h(r_{13}) c(r_{32}) \quad (38)$$

or, equivalently,

$$\tilde{h}(k) - \tilde{c}(k) = \rho \int d\mathbf{r}_{13} e^{i\mathbf{k}\cdot\mathbf{r}_{13}} h(r_{13}) \int d\mathbf{r}_{32} e^{i\mathbf{k}\cdot\mathbf{r}_{32}} c(r_{32}), \quad (39)$$

given that

$$\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2 = \mathbf{r}_1 - \mathbf{r}_3 - (\mathbf{r}_2 - \mathbf{r}_3). \quad (40)$$

Eq. (39) can be written as

$$\tilde{h}(k) - \tilde{c}(k) = \rho \tilde{h}(k) \tilde{c}(k) \quad (41)$$

or

$$[1 + \rho \tilde{h}(k)] [1 - \rho \tilde{c}(k)] = 1. \quad (42)$$

For our system, the first factor, $1 + \rho \tilde{h}(k)$, is a bounded function with no poles in the real k -axis. Therefore, $1 - \rho \tilde{c}(k)$ has no zeros on the real k -axis. Because of the spherical symmetry of $c(r)$, $\tilde{c}(k) = \tilde{c}(-k)$, that is, $\tilde{c}(k)$ is an even function of k . Thus, using the Wiener-Hopf factorization theorem [4], $1 - \rho \tilde{c}(k)$ can be factored as

$$1 - \rho \tilde{c}(k) = [1 - \rho \tilde{Q}(k)] [1 - \rho \tilde{Q}(-k)], \quad (43)$$

where $\tilde{Q}(k)$ has no zeros in the upper complex half plane and $\tilde{Q}(-k)$ has no zeros in the lower complex half plane. Since $\tilde{c}(k)$ is an entire function, $\tilde{Q}(k)$ must be entire also. Notice that the property (43) is nothing really special. It is simply the square root property: any even function of k can be written as

$$f(k^2) = \prod_{i=1}^{\infty} e^{i\phi} (a_i^+ - k)(a_i^- - k) e^{-i\phi}.$$

For example,

$$\begin{aligned} \cos k &= c \prod_{n=1}^{\infty} \left[\frac{\pi}{2} (2n+1)^2 + k^2 \right] \\ &= \left\{ \prod_{n=1}^{\infty} \left[ik + \frac{2n+1}{2} \pi \right] \right\} \left\{ \prod_{n=1}^{\infty} \left[-ik + \frac{2n+1}{2} \pi \right] \right\}. \end{aligned}$$

The factorization then is really taking a square root and, as such, is not uniquely defined. Now, substituting (43) into (42) in the form

$$[1 + \rho \tilde{h}(k)] [1 - \rho \tilde{Q}(k)] = \frac{1}{1 - \rho \tilde{Q}(-k)} \tag{44}$$

and taking the inverse Fourier transform. We have for the right hand side of Eq. (44)

$$\frac{1}{2\pi i} \oint \frac{dk e^{-ikr}}{1 - \rho \tilde{Q}(k)} = 0, \tag{45}$$

where we have closed the circuit through the lower half k -plane, where $1 - \rho \tilde{Q}(k)$ has no zeros. This means that the function has no poles and, for that reason, the integral must be zero. The other member of Eq. (44),

$$\frac{1}{2\pi} \int dk e^{ikr} [1 + \rho \tilde{h}(k) - \rho \tilde{Q}(k) - \rho^2 \tilde{h}(k) \tilde{Q}(k)] = \delta(r), \tag{46}$$

must be computed term by term:

$$\frac{1}{2\pi} \int dr e^{-ikr} \int dr_1 e^{ikr_1} J(r_1) = \int dr_1 J(r_1) \delta(r - r_1) = J(r). \tag{47}$$

We finally get, using (36),

$$J(r) = Q(r) + \rho \int_0^R dr_1 J(|r - r_1|) Q(r_1), \quad r > 0. \tag{48a}$$

Fourier inversion of the defining equation for $Q(r)$ (43) yields, using (32),

$$S(r) = Q(r) - \rho \int dr_1 Q(r_1) Q(r_1 - r). \tag{48b}$$

We need to solve the Eqs. (48) to find the unknown factor function $Q(r)$. The first property of $Q(r)$ is that it must be of the same range as $c(r)$. Remembering (43) and the fact that the factor functions are defined only for $0 < r \leq R$:

$$\begin{aligned} 2\pi \int_r^R ds sc(s) &= Q(r) - \rho \int_r^R dr_1 Q(r_1)Q(r_1 - r) \\ &= 0, \quad \text{for } r > R, \end{aligned} \quad (49)$$

which necessarily requires that

$$Q(r) = 0, \quad \text{for } r \geq R. \quad (50)$$

We need to consider (48a) only for $r < R$. In that case, because of the definition of $J(r)$ [Eq. (37)], and the boundary condition Eq. (30), we have for $r < R$

$$J(r) = 2\pi \int_r^\infty ds sh(s) = -2\pi \int_r^R ds s + 2\pi \int_R^\infty ds sh(s) \quad (51a)$$

$$= \pi(r^2 - R^2) + b_0, \quad \text{for } r < R, \quad (51b)$$

then, by taking successive derivatives ($Q'(r) = dQ/dr$), we can show that $Q(r)$ must be a polynomial of the second degree, since

$$Q'''(r) = 0, \quad (52)$$

and that, to conform to (50), it must be of the form

$$Q(r) = (r - R) \left[\frac{1}{2} r \alpha + \beta \right]. \quad (53)$$

To find the actual values of the coefficients α and β we take successive derivatives of (48a):

$$2\pi r = Q'(r) + 2\pi\rho \int_0^R dr_1 (r - r_1)Q(r_1), \quad (54)$$

$$2\pi = Q''(r) + 2\pi\rho \int_0^R dr_1 Q(r_1). \quad (55)$$

Now,

$$\int_0^R dr_1 Q(r_1) = -\frac{R^2\beta}{2} - \frac{R^3\alpha}{12}, \quad (56)$$

$$\int_0^R dr_1 r_1 Q(r_1) = -\frac{R^3\beta}{6} - \frac{R^4\alpha}{24}. \quad (57)$$

So that, if we take $r = R/2$ in (54), we get

$$\pi R = Q'(R/2) + 2\pi\rho \left[-\frac{R^3\beta}{12} \right], \quad (58)$$

but $Q'(R/2) = \beta$, so that

$$\beta = \frac{\pi R}{\Delta}, \quad \text{with } \Delta = 1 - \frac{\rho R^3\pi}{6}, \quad (59)$$

where Δ is the fraction of volume not occupied by the hard spheres. Eq. (55) yields

$$2\pi = \alpha + 2\pi\rho \left[-\frac{R^2\beta}{2} - \frac{R^3\alpha}{12} \right], \quad (60)$$

$$\alpha = \frac{2\pi}{\Delta} \left[1 + \frac{\rho R^2\beta}{2} \right] = \frac{2\pi}{\Delta} \left[1 + \frac{\pi\rho R^3}{2\Delta} \right], \quad (61)$$

which completes our solution. To compute the pair correlation functions, we simply substitute $Q(r)$ into Eqs. (48).

To compute the pair correlation function (or radial distribution function) $g(r)$ we take

$$2\pi r h(r) = 2\pi\rho \int_0^R dr_1 h(r-r_1)g(r-r_1)Q(r_1), \quad r > R, \quad (62)$$

to which we add the analytic continuation of (54) for $r > R$. Remembering that $g(r) = h(r) + 1$, Eq. (25), we obtain

$$2\pi r g(r) = Q'(r) + \int_0^{r-R} dr_1 h(r-r_1)g(r-r_1)Q(r_1), \quad (63)$$

which can be solved numerically (see Fig. 2, Appendix and Ref. [14]).

It will be interesting to notice that when $r = R$

$$2\pi R g(R) = Q'(R) = \beta + \frac{R\alpha}{2}. \quad (64)$$

The result shows layering of the spheres around the central one. The short range structure in a dense fluid is similar to that of a close packed solid, but it is quickly washed out. The PY theory is quite good in representing the pair correlation function of a hard core fluid, as can be seen by comparing with computer simulations [5,9,12,16].

An equivalent treatment is made to solve the more general case of a mixture of hard spheres [17,18].

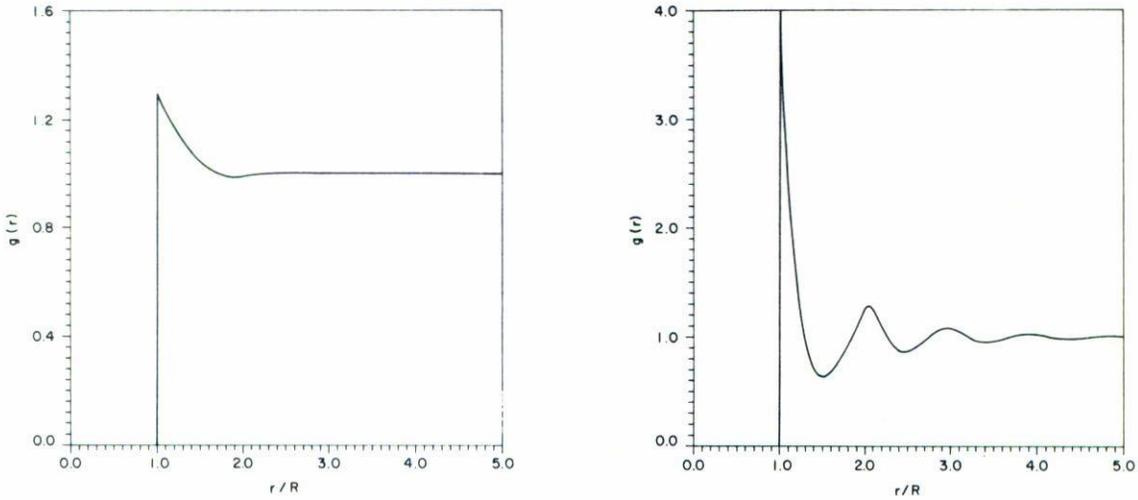


FIGURE 2. The radial distribution function for a HS system for two different reduced densities: a) $\eta = 0.1$ and b) $\eta = 0.4469$. In both we take $x = r/R$, where r is the distance between two hard spheres and R is their diameter.

Some thermodynamic quantities of fluid systems whose interaction potential is known can be written in terms of the radial distribution function and also, as we will see, in terms of the FCF's of Baxter [9,13].

4. THERMODYNAMIC PROPERTIES OF HARD SPHERES (HS) AND STICKY HARD SPHERES (SHS) SYSTEMS

In this section we deduce some thermodynamic quantities for a single hard spheres system following the formalism of Baxter's original work.

First, we deduce the mean energy U in the grand canonical ensemble

$$\begin{aligned}
 U &= \frac{1}{\Theta} \sum_{N=1}^{\infty} \frac{z^N}{N!} \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{\beta U_N} \left\{ \frac{3}{2} N k T + \sum u_{ij}(\mathbf{r}) \right\} \\
 &= \frac{3}{2} \langle N \rangle k T + \frac{1}{2\Theta} \sum \frac{z^N}{(N-2)!} \int \cdots \int d\mathbf{r}_1 \cdots d\mathbf{r}_N \phi_{12}(\mathbf{r}) e^{-\beta U_N},
 \end{aligned}$$

therefore

$$u_N \equiv \frac{U}{\langle N \rangle} = \frac{3}{2} k T + \frac{1}{2} \rho \int d\mathbf{r} \phi(\mathbf{r}) g(\mathbf{r}), \quad (65)$$

where the first term is the mean energy of a ideal gas and the second term is called the excess energy [9,7,17].

If we derive the grand partition function (6) with respect to the volume V , we can find the known virial pressure [6]

$$V \frac{\partial \Theta}{\partial V} \Big|_{m,T} = \int d\mathbf{r}_1 \rho_i(\mathbf{r}_1) - \frac{1}{6} \int d\mathbf{r}_1 d\mathbf{r}_2 \phi'_{ij}(|\mathbf{r}_1 - \mathbf{r}_2|) \rho_{ij}(\mathbf{r}_1, \mathbf{r}_2)$$

or, considering (10) and (11) and the limiting case $V \rightarrow \infty$,

$$P\beta = \rho - \frac{2\pi\rho^2}{3} \int dr r^3 \phi'(r)g(r), \tag{66}$$

where ϕ' is the derivative with respect to r .

From the thermal compressibility coefficient

$$K_T = \frac{1}{\rho} \frac{\partial \rho}{\partial P} \Big|_{V,T},$$

the state equation for the grand canonical ensemble $PV\beta = \log \Theta$, and Eq. (10), we can obtain directly [9,17]

$$k_B T \frac{\partial \rho}{\partial P} \Big|_{V,T} = \frac{\partial \langle N \rangle}{\partial (\log \Theta)} \Big|_{V,T} = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}. \tag{67}$$

We can easily show that [9]

$$\int \dots \int d\mathbf{r}_1 \dots d\mathbf{r}_L \rho(\mathbf{r}_1, \dots, \mathbf{r}_L) = \left\langle \frac{N!}{(N-L)!} \right\rangle$$

and we can rewrite (67) as

$$kT \frac{\partial \rho}{\partial P} \Big|_{V,T} = 1 + \rho \int dr h(r), \tag{68}$$

and by the fact that the integral in (68) is $\tilde{h}(0)$ [9,17], we get

$$\frac{1}{k_B T} \frac{\partial \rho}{\partial P} \Big|_{V,T} = \{ \tilde{Q}(0) \}^2. \tag{69}$$

This latter equation can be integrated over ρ or $\eta \equiv \pi\rho R^3/6$ to obtain the compressibility state equation for a hard-sphere fluid system [9,16,17]:

$$\frac{P}{\rho k_B T} = \frac{1 + \eta + \eta^2}{(1 - \eta)^3}. \tag{70}$$

Now we are going to discuss a second model, for which the PYA gives an analytic solution, called sticky hard-spheres (SHS) system. For the monodisperse SHS system Baxter has proposed an analytical form for the sticky potential [11]:

$$\beta\phi(r) = \begin{cases} +\infty, & 0 < r < R', \\ \log \left[\frac{12\tau(R-R')}{R} \right], & R' < r < R, \\ 0, & r > R, \end{cases} \quad (71)$$

where τ is an adimensional measurement of temperature, being zero for zero temperature and taking higher values when the temperature increases. This potential model contains two of the most important ingredients of a real molecular interaction, namely, a harsh repulsion and an attraction, and yet is the only potential, with these properties, for which the PY approximation has been solved analytically. We consider in this work the limit $R' \rightarrow R$.

For this system, the Mayer function, [Eq. (14)], takes the form

$$f(r) = \begin{cases} -1 + \frac{R'\delta(r-R')}{12\tau}, & \text{for } 0 < r < R, \\ 0, & \text{for } r > R, \end{cases} \quad (72a)$$

and the total correlation function is

$$h(r) = \begin{cases} -1 + \frac{\lambda R'\delta(r-R')}{12}, & \text{for } R' < r < R, \\ 0, & \text{for } 0 < r < R', \end{cases} \quad (72b)$$

with λ a parameter to be determined below [20]. Following the same procedure as for the hard-spheres case, we find that the FCF can be written as

$$Q(r) = \frac{\alpha}{2}(r^2 - R^2) + \beta R(r - R) + \frac{\lambda R^2}{12}, \quad (73)$$

where

$$\alpha = \frac{1 + 2\eta - \mu}{(1 - \eta)^2}, \quad \beta = \frac{\mu - 3\eta}{2(1 - \eta)^2}, \quad (74)$$

and the μ and η parameters are defined as

$$\eta = \frac{\pi\rho R^2}{6}, \quad \mu = \lambda\eta(1 - \eta), \quad (75)$$

with λ an adimensional parameter.

The PY approximation can be written as

$$1 + h(r) = [1 + f(r)]y(r), \tag{76}$$

where $y(r)$ is defined by

$$y(r) = 1 + h(r) - c(r), \tag{77}$$

which is a continuous function in the limit $R' = R$. One can take the limiting forms of $f(r)$ and $h(r)$, [Eqs. (72a) and (72b)], and then obtain, for the PY approximation, using the Eqs. (76) and (77):

$$y(R) = \lambda\tau = \alpha + \beta + \frac{Q(0)\eta\lambda}{R^2}$$

or

$$\lambda\tau = \frac{1 + \eta/2}{(1 - \eta)^2} - \frac{\eta\lambda}{1 - \eta} + \frac{\eta\lambda^2}{12}. \tag{78}$$

This equation determines the behavior of λ [9,19].

The compressibility state equation for the SHS system can be obtained, again, from Eq. (69) with the definitions of Eq. (75)

$$\frac{P}{\rho k_B T} = \frac{1 + \eta + \eta^2 - \mu(1 + \eta/2) + \frac{\mu^3}{36\eta}}{(1 - \eta)^3}. \tag{79}$$

Notice that if we make $\lambda = 0$ we get again the state equation for HS Eq. (70): λ is a measurement of stickiness.

The state equation for HS in the PY approximation [Eq. (70)] is well compared with the obtained by another approximations [5]. In the SHS case a phase transition can be observed due to the complex values of the stickiness parameter λ [9,19].

APPENDIX

Using the algorithm of Perram [14], one can plot the total correlation function (or the radial distribution function) for different concentrations:

```

/*****\

Implementation of Perram's method for the
evaluation of h(x) and g(x) (with x=r/R).

Monodisperse hard-spheres case.
    
```

```

R = hard sphere diameter
teta = r . h(r)
x = r/R
q(x) = Baxter's function
dq(x)= derivative of Baxter's functions

```

```
Language: Turbo C++
```

```

\*****/

#include <math.h>
#include <stdio.h>
#include <conio.h>
#include <ftool.h>

/* variables declaration */

double eta;          // packing fraction
double teta[500];   // defined function as r . h(r) for r outside
of integration range
double x[500];      // x=r/R is the relative distance from hard
sphere core
double h[500];      // values of the total correlation function
double g[500];      // values of the radial distribution function
double qx[100];     // values of q(x) between 0 and 1
double delta;       // increments of x=n . delta
int regions;        // number of intervals from 1.0
int n_int;          // number of divisions of 1
FILE *fopen(),
      *tdata,       // teta(x) values file
      *hdata,       // h(x) values file
      *gdata;       // g(x) values file

/* function declarations */

double q(double x);
double dq(double x);
double A1(double eta);
double A2(double eta);

/* main program */

main()
{
    int k;

    clrscr();
    printf("\n Reduced density: ");
    eta = read_flt(0,0,8);
    printf("\n Number of regions (from x=1.0): ");
    regions = read_int(0,0,2);
    printf("\n Number of divisions of 1.0: ");
    n_int = read_int(0,0,3);

```

```

delta = 1.0/(n_int);

/* evaluation of x, q(x), teta(x) and h(x) in (0,1-delta) */
k = 0;
do {
  x[k] = k*delta;
  qx[k] = q(x[k]);
  teta[k] = -x[k];
  h[k] = -1.0; /* = teta[k]/x[k] */
  g[k] = h[k] + 1;
} while (++k <= n_int);

/* contact values of x, q(x), teta(x) and h(x) */
x[n_int] = 1.0;
qx[n_int] = 0.0;
teta[n_int] = dq(x[n_int]) - 1;
h[n_int] = teta[n_int]/x[n_int];
g[n_int] = h[n_int] + 1;

/* values of x, q(x), teta(x) and h(x) for x>1.0 */
/* Perram's algorithm */
k = 1;
do {
  int s = 1; double sum = 0.0;
  do {
    sum += qx[s]*teta[n_int+k-s];
  } while (++s < n_int);
  x[n_int+k] = (n_int+k)*delta;
  teta[n_int+k] = 12*eta*delta/(1-6.0*eta*delta*qx[0])*sum;
  h[n_int+k] = teta[n_int+k]/x[n_int+k];
  g[n_int+k] = h[n_int+k] + 1;
} while (++k <= regions*n_int);
tdata = fopen("perrt.dat","w");
hdata = fopen("perrh.dat","w");
gdata = fopen("perrg.dat","w");

/* data to files */
/* values of correlation functions in x=1- */
fprintf(tdata,"%8.3f %8.3f \n",1.0,-1.0);
fprintf(hdata,"%8.3f %8.3f \n",1.0,-1.0);
fprintf(gdata,"%8.3f %8.3f \n",1.0,0.0);
/* values of correlation functions for x>1.0 */
for (k = n_int; k <= (regions+1)*n_int; k++) {
  printf("\n x=%8.3f, $\theta$=%8.3f, h(x)=%8.3f,
  g(x)=%8.3f",x[k],teta[k],h[k],g[k]);
  fprintf(tdata,"%8.3f %8.3f \n",x[k],teta[k]);
  fprintf(hdata,"%8.3f %8.3f \n",x[k],h[k]);
  fprintf(gdata,"%8.3f %8.3f \n",x[k],g[k]); }
fclose(tdata);
fclose(hdata);
fclose(gdata);
}

```

```

double q(double x)
{ return 0.5*A1(eta)*(x*x-1)+A2(eta)*(x-1); }

double dq(double x)
{ return A1(eta)*x+A2(eta); }

double A1(double eta)
{ return (1.0+2.0*eta)/pow((1.0-eta),2); }

double A2(double eta)
{ return (-1.5*eta)/pow((1.0-eta),2); }

```

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