



# Direct correlation functions and bridge functions in additive hard-sphere mixtures

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A method to obtain (approximate) analytical expressions for the radial distribution functions in a multicomponent mixture of additive hard spheres that was recently introduced is used to obtain the direct correlation functions and bridge functions in these systems. This method, which yields results practically equivalent to the generalized mean spherical approximation and includes thermodynamic consistency, is an alternative to the usual integral equation approaches and requires as input only the contact values of the radial distribution functions and the isothermal compressibility. Calculations of the bridge functions for a binary mixture using the Boublik–Mansoori–Carnahan–Starling–Leland equation of state are compared to parallel results obtained from the solution of the Percus–Yevick equation. We find that the conjecture recently proposed by Guzmán and del Río (1998, *Molec. Phys.*, **95**, 645), stating that the zeros of the bridge functions occur approximately at the same value of the shifted distance for all pairs of interactions, is at odds with our results. Moreover, in the case of disparate sizes, even the Percus–Yevick bridge functions do not have this property. It is also found that the bridge functions are not necessarily non-positive.

## 1. Introduction

Integral equation theories for the description of thermodynamic and structural properties of liquids usually lead to qualitatively satisfactory results. Nonetheless, in general they involve hard numerical labour as well as criteria to formulate the closure relations that are not clearcut. This is true even for the simplest and most studied systems, namely the pure hard-sphere fluid and hard-sphere fluid mixtures. Therefore, it is not surprising that many attempts at providing general features, symmetries, approximations or parametrizations of the so-called bridge functions have been reported in the literature [1–11]. These bridge functions enter in the closure relations and are defined as the sum of elementary diagrams (whose precise computation is a formidable and rather difficult task); they account for some molecular spatial correlations of higher order than pair correlations. Of course the availability of the analytical results provided by the Percus–Yevick (PY) theory [12] in the case of the pure hard-sphere fluid [13] and hard-sphere fluid mixtures [14] allows one to determine explicitly the bridge functions in this instance, but they inherit the (theoretically) unpleasant lack of thermodynamic consistency as well as the limited den-

sity range of applicability involved in the PY approximation.

In a related context, it is worth pointing out that in the pioneering work of Rosenfeld and Ashcroft [15] it was found that an important class of pair potentials shared the property that their corresponding bridge functions were remarkably similar to each other and to the hard-sphere bridge function. This observation led to the common form of the reference-hypernetted chain theory [16], considered by many to be perhaps the most accurate theory for the structural properties of fluids, in which the bridge functions of the system of interest are equated to those of a hard-sphere system. Thus, the search for accurate and relatively simple approximations for the bridge functions of a pure hard-sphere fluid and hard-sphere fluid mixtures has been pursued in the last few years. Notable among the results of this pursuit are the empirical parametrization due to Malijevský and Labík (ML) for the hard-sphere fluid and its recent extension to binary hard-sphere mixtures [17]. These involve a careful and thorough analysis of a large set of computer simulation data. Some apparent regularities of the bridge functions in the case of binary mixtures (present in the PY results and in recent simulation data of Malijevský *et al.* [18]) has been recently suggested by Guzmán and del Río [19]. If these regularities were to hold in general, they would allow one to simplify the ML parametrization and would

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serve as a starting point for considering hard-sphere mixtures with three or more components. Due to the scarcity of simulation data for mixtures, the suggestion currently remains merely conjecture.

Notwithstanding the merits of all these theoretical and semi-empirical efforts, it is clear that, especially in the case of mixtures, the scarcity of results and the relatively slow progress reflect the amount and difficulty of the numerical work that has to be done to obtain them. Therefore, one may reasonably wonder whether an alternative theoretical approach, that at least avoided the inherent difficulty of solving nonlinear integral equations, would also provide information on the bridge functions of the pure hard-sphere fluid and hard-sphere mixtures. It is the major aim of this paper to provide an affirmative answer to the foregoing question.

In previous work [20, 21] we have introduced a method to analytically derive (approximate) expressions for the radial distribution functions and structure factors of fluids and fluid mixtures. This method rests on a completely different philosophy than the one involved in integral equation theories and thus is totally void of the difficulty associated with providing any particular closure. In the case of pure hard-sphere fluids and hard-sphere mixtures and in the lowest order of approximation, it yields the well known PY results. Furthermore and by construction, our expressions in the next order of approximation, which yields results practically equivalent to those of the generalized mean spherical approximation (GMSA) [22] but is much simpler to implement, also embody thermodynamic consistency. As shown below, by using such radial distribution functions in connection with the Ornstein–Zernike (OZ) equation it is rather straightforward to derive the direct correlation functions and, in turn, the bridge functions of the system, this latter for distances greater than the contact distance.

The organization of the paper is as follows. In section 2 we outline the main ideas of our method to obtain the radial distribution functions of an  $N$ -component mixture of additive hard spheres. For this mixture the Boublík–Mansoori–Carnahan–Starling–Leland (BMCSL) [23] equation of state and the Grundke–Henderson–Lee–Levesque (GHLL) [24, 25] contact values of the radial distribution functions, which yield the BMCSL equation of state, are assumed to hold. If  $N$  is set equal to one then the pure hard-sphere fluid case readily follows. Expressions for the direct correlation functions are given there. Section 3 provides an analysis of the bridge functions as well as a comparison with previous work. We close the paper in section 4 with further discussion and some concluding remarks.

## 2. The radial distribution functions, the direct correlation functions and the bridge functions of a hard-sphere mixture

In this section we outline a method to obtain (approximate) analytical expressions for the radial distribution functions  $g_{ij}(r)$  of a multicomponent hard-sphere mixture. It consists of an extension to mixtures of the method previously applied to one-component systems of hard spheres, sticky hard spheres and square wells [20]. For details the reader may refer to [21].

An  $N$ -component mixture made of  $\rho_i$  hard spheres (of diameter  $\sigma_i$ ) per volume unit may be characterized by  $2N - 1$  parameters (for instance, the  $N - 1$  molar fractions  $x_i$ , the  $N - 1$  size ratios  $\sigma_i/\sigma_1$  and the packing fraction  $\eta = (\pi/6) \sum_i \rho_i \sigma_i^3$ ) and involves  $N(N + 1)/2$  radial distribution functions  $g_{ij}(r)$ .

As happens in the PY and GMSA theories, it is convenient to work in the Laplace space and define

$$G_{ij}(s) = \int_0^\infty dr \exp(-sr) r g_{ij}(r). \quad (1)$$

There are two basic requirements that  $G_{ij}(s)$  must satisfy. First, since  $g_{ij}(r) = 0$  for  $r < \sigma_{ij}$ , with  $\sigma_{ij} = (\sigma_i + \sigma_j)/2$ , and  $g_{ij}(\sigma_{ij}^+) = \text{finite}$ , this implies that (i)  $\lim_{s \rightarrow \infty} s \exp(s\sigma_{ij}) G_{ij}(s) = \text{finite}$ . Second, the isothermal compressibility  $\kappa_T = \text{finite}$ , so that (ii)  $\lim_{s \rightarrow 0} [G_{ij}(s) - s^{-2}] = \text{finite}$ . The approximation we will use consists of assuming the following functional form:

$$G_{ij}(s) = \frac{\exp(-s\sigma_{ij})}{2\pi s^2} \sum_k L_{ik}(s) [(1 + \alpha s) \mathbf{I} - \mathbf{A}(s)]^{-1}_{kj}, \quad (2)$$

where  $\mathbf{I}$  is the  $N \times N$  unit matrix,

$$L_{ij}(s) = L_{ij}^{(0)} + L_{ij}^{(1)} s + L_{ij}^{(2)} s^2 \quad (3)$$

and

$$A_{ij}(s) = \rho_i \sum_{n=0}^2 \varphi_n(s\sigma_i) \sigma_i^{n+1} L_{ij}^{(2-n)}, \quad (4)$$

with

$$\varphi_n(x) \equiv x^{-(n+1)} \left[ \sum_{m=0}^n \frac{(-x)^m}{m!} - \exp(-x) \right]. \quad (5)$$

Condition (i) is verified by construction. On the other hand, condition (ii) yields two *linear* sets of  $N^2$  equations each, whose solution is straightforward, namely

$$L_{ij}^{(0)} = \lambda + \lambda' \sigma_j + 2\lambda' \alpha - \lambda \sum_k \rho_k \sigma_k L_{kj}^{(2)}, \quad (6)$$

$$L_{ij}^{(1)} = \lambda \sigma_{ij} + \frac{\lambda'}{2} \sigma_i \sigma_j + (\lambda + \lambda' \sigma_i) \alpha - \frac{\lambda}{2} \sigma_i \sum_k \rho_k \sigma_k L_{kj}^{(2)}, \quad (7)$$

where  $\lambda \equiv 2\pi/(1 - \eta)$  and  $\lambda' \equiv (\lambda/2)^2 \sum_k \rho_k \sigma_k^2$ .

The parameters  $L_{ij}^{(2)}$  and  $\alpha$  (which play a role similar to that of the parameters  $K_{ij}$  and  $z$  in the GMSA) are arbitrary, so that conditions (i) and (ii) are satisfied regardless of their choice. In particular, if one chooses  $L_{ij}^{(2)} = \alpha = 0$ , our approximation coincides with the PY solution. If, on the other hand, we fix given values for  $g_{ij}(\sigma_{ij}^+)$ , we get the relationship

$$L_{ij}^{(2)} = 2\pi\alpha\sigma_{ij}g_{ij}(\sigma_{ij}^+). \quad (8)$$

Thus, only  $\alpha$  remains to be determined. Finally, if we fix  $\kappa_T$ , we obtain a closed equation for  $\alpha$  of degree  $2N$ . It is worth pointing out that in the particular case of a pure hard-sphere fluid ( $N = 1$ ) one gets a quadratic algebraic equation for  $\alpha$ , while for a binary mixture ( $N = 2$ ) the *explicit* knowledge of  $G_{ij}(s)$  only requires one to solve a quartic equation, which also has an *analytical* solution. A natural choice to close the scheme, which we will of course consider in this paper, is to take the GHLL values [24, 25] of  $g_{ij}(\sigma_{ij}^+)$ , as well as the corresponding BMCSL [23] isothermal compressibility  $\kappa_T$ . But other possibilities are available and one of them will also be addressed later on. Once  $G_{ij}(s)$  has been determined, inverse Laplace transformation directly yields  $rg_{ij}(r)$ , while the Fourier transforms  $\tilde{h}_{ij}(q)$  of the total correlation functions  $h_{ij}(r)$  readily follow from the relation

$$\begin{aligned} \tilde{h}_{ij}(q) &\equiv \int d\mathbf{r} \exp(i\mathbf{q} \cdot \mathbf{r}) h_{ij}(r) \\ &= -2\pi \frac{G_{ij}(s) - G_{ij}(-s)}{s} \Big|_{s=iq}, \end{aligned} \quad (9)$$

where  $i$  is the imaginary unit. In Fourier space and introducing the quantities  $\hat{H}_{ij}(q) = (\rho_i \rho_j)^{1/2} \tilde{h}_{ij}(q)$  and  $\hat{C}_{ij}(q) = (\rho_i \rho_j)^{1/2} \tilde{c}_{ij}(q)$  the OZ equation reads

$$\hat{\mathbf{C}}(q) = \hat{\mathbf{H}}(q) \cdot [\mathbf{I} + \hat{\mathbf{H}}(q)]^{-1}, \quad (10)$$

so that after replacement of  $\hat{\mathbf{H}}(q)$  and subsequent inverse Fourier transformation it is straightforward to get  $c_{ij}(r)$ . The result gives  $c_{ij}(r)$  for  $r > \sigma_{ij}$  as the superposition of  $N$  Yukawas (see the Appendix):

$$c_{ij}(r) = \sum_{\ell=1}^N \frac{K_{ij}^{(\ell)}}{r} \exp[-z_\ell(r - \sigma_{ij})], \quad (11)$$

where  $q = \pm i z_\ell$  with  $\ell = 1, \dots, N$  are the zeros of  $\det[\mathbf{I} + \hat{\mathbf{H}}(q)]$  and the amplitudes  $K_{ij}^{(\ell)}$  are obtained by applying the residue theorem as

$$K_{ij}^{(\ell)} = \frac{i z_\ell}{2\pi} \exp(-z_\ell \sigma_{ij}) \lim_{q \rightarrow i z_\ell} \tilde{c}_{ij}(q)(q - i z_\ell). \quad (12)$$

Finally, we note that the bridge functions  $B_{ij}(r)$  for  $r > \sigma_{ij}$  are linked to  $g_{ij}(r)$  and  $c_{ij}(r)$  through

$$B_{ij}(r) = \ln g_{ij}(r) - g_{ij}(r) + c_{ij}(r) + 1. \quad (13)$$

Equations (11) and (13), after replacement of the results for  $g_{ij}(r)$ , will be used below to investigate some properties of the bridge functions  $B_{ij}(r)$  in pure hard-sphere fluids and hard-sphere mixtures.

### 3. Comparison with other results

We begin with the pure hard-sphere fluid, that is, we now consider the case when  $N = 1$ . For this system a variety of closures to the OZ equation are available [2–7], for instance

$$B^{\text{PY}}(r) = \ln[1 + \gamma(r)] - \gamma(r), \quad (14)$$

$$B^{\text{HNC}}(r) = 0, \quad (15)$$

$$B^{\text{VM}}(r) = -\frac{[\gamma(r)]^2}{2\{1 + a_1\gamma(r)\}}, \quad (16)$$

$$B^{\text{MS}}(r) = [1 + 2\gamma(r)]^{1/2} - \gamma(r) - 1, \quad (17)$$

$$B^{\text{RY}}(r) = \ln \left\{ 1 + \frac{\exp\{[1 - \exp(-a_2 r)]\gamma(r)\} - 1}{1 - \exp(-a_2 r)} \right\} - \gamma(r), \quad (18)$$

$$B^{\text{BPGG}}(r) = [1 + a_3\gamma(r)]^{1/a_3} - \gamma(r) - 1, \quad (19)$$

where  $\gamma(r) \equiv g(r) - c(r) - 1$  and the labels HNC, VM, MS, RY and BPGG denote the hypernetted-chain [2], Verlet modified [3], Martynov–Sarkisov [4], Rogers–Young [5] and Ballone–Pastore–Galli–Gazzillo [6] closures, respectively, and the adjustable parameters  $a_i$  ( $i = 1, 2, 3$ ) have been estimated to take the values  $a_2 = 0.160$  [5],  $a_1 = 4/5$  and  $a_3 = 15/8$  [9]. It is at this point interesting to analyse to what extent the bridge functions calculated upon substitution in such closures of our expressions for the radial distribution function and direct correlation function differ or are compatible with the actual bridge function computed using equation (13). To this end, we introduce the quantity  $\Delta B^*(r) \equiv B^*(r) - B(r)$ , where the asterisk refers to a given label. Notice that in particular  $\Delta B^{\text{HNC}}(r) = -B(r)$  and  $\Delta B^{\text{PY}}(r) = \ln[1 - c(r)/g(r)]$ . In figure 1 we display the behaviour of  $\Delta B^*(r)$  as a function of the shifted distance  $r - \sigma$  for a packing fraction  $\eta = 0.49$ , i.e. close to the

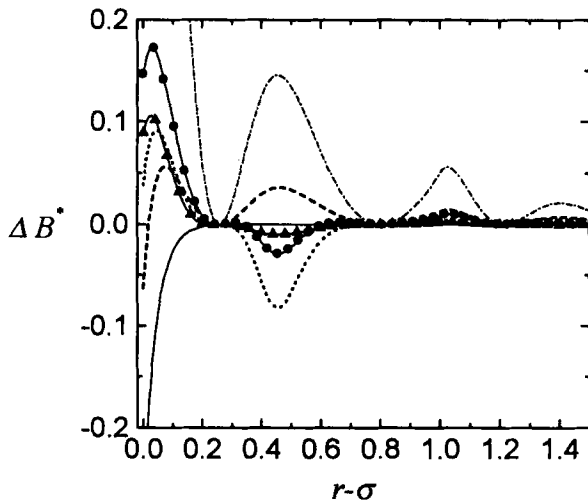


Figure 1. The difference  $\Delta B^*(r)$  as a function of the shifted distance  $r - \sigma$  for a simple hard-sphere fluid with  $\eta = 0.49$  and  $\sigma = 1$ , according to various closures: HNC (dash-dotted line), PY (solid line), RY (dashed line), MS (dotted line), VM (solid line with triangles) and BPGG (solid line with circles).

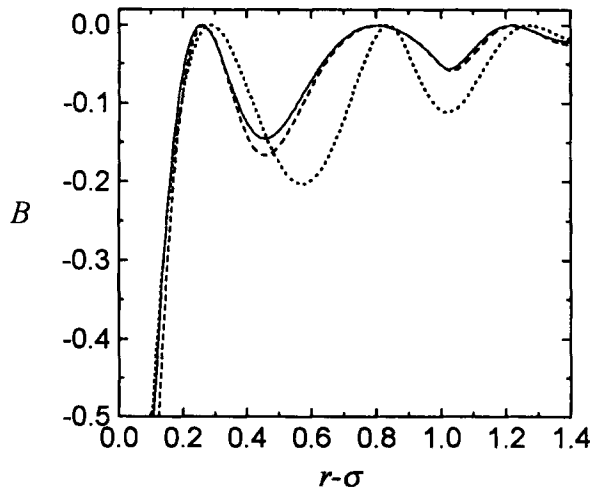


Figure 2. Bridge function  $B(r)$  versus  $r - \sigma$  for a simple hard-sphere fluid with  $\eta = 0.49$  and  $\sigma = 1$ . Solid line: present method; dashed line: PY results; dotted line: ML parametrization.

freezing transition. Clearly the main discrepancies between both types of calculation show up near the contact point, but one could reasonably argue that the RY, the MS and the VM closures are rather compatible with the result of the present approach in that region.

Figure 2 displays the results for the bridge function as obtained with the PY theory, the parametrization of Malijevský and Labík (ML) [17] and our formulation, again for the packing fraction  $\eta = 0.49$ . As clearly seen in the figure, the discrepancy between the results of the

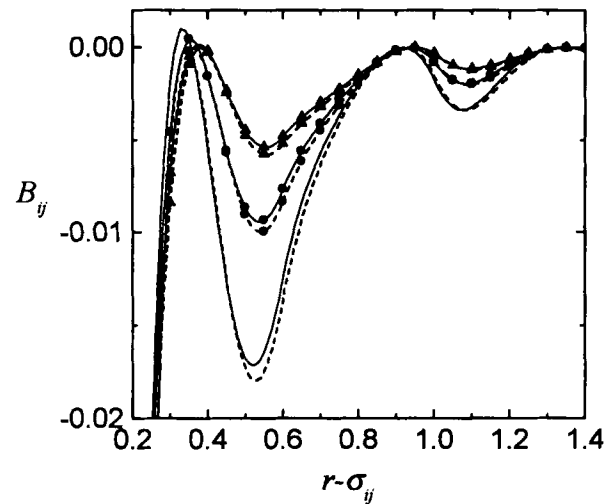


Figure 3. Bridge functions  $B_{ij}(r)$  versus  $r - \sigma_{ij}$  for an equimolar binary mixture of hard spheres with  $\eta = 0.35$  and diameters  $\sigma_2 = 0.6$  and  $\sigma_1 = 1$ . Solid lines: present method; dashed lines: PY results. The curves for  $B_{11}(r)$  contain no symbols, those for  $B_{12}(r)$  contain circles and the ones for  $B_{22}(r)$  contain triangles.

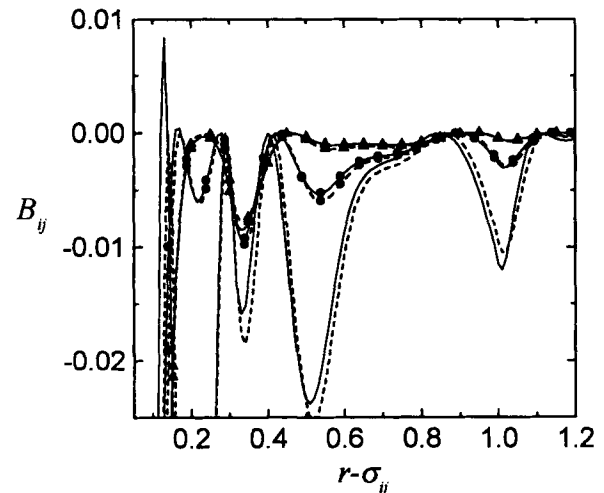


Figure 4. Bridge functions  $B_{ij}(r)$  versus  $r - \sigma_{ij}$  for a binary mixture of hard spheres with  $\eta = 0.49$ , molar fraction  $x_1 = 1/16$  and diameters  $\sigma_2 = 0.3$  and  $\sigma_1 = 1$ . The code for the different curves is as in figure 3.

parametrization and both ours and those of the PY theory is rather significant. Also, although not perceptible on the scale of the figure, we note that in our case the first maximum of the bridge function attains a positive value, whereas both the ML parametrization and the PY theory always lead to non-positive values for the bridge function. We will come back to this point later on.

We now turn to binary mixtures. In figures 3 and 4 results for the different bridge functions are shown for

two cases. In figure 3, which corresponds to the case examined by Guzmán and del Río [19], it is an equimolar mixture with  $\eta = 0.35$  and  $\sigma_2/\sigma_1 = 0.6$ ; the second mixture is defined by  $\eta = 0.49$ ,  $x_1 = 1/16$ ,  $x_2 = 15/16$  and  $\sigma_2/\sigma_1 = 0.3$ . We have also included in these figures the results obtained with the PY approximation. The differences between the results of both approaches are particularly important in the first maximum of the bridge functions and once more in our case we get some intervals of positive values. These figures also illustrate the fact that the phase-shift symmetry that was recently conjectured by Guzmán and del Río [19] to hold on the basis of the behaviour observed in figure 3, is not even present in the PY theory, particularly at short distances, and this becomes more evident as the disparity in size ratio is increased, as shown in figure 4.

As another illustration, in figures 5 and 6 we display results for a ternary mixture where  $\eta = 0.49$ ,  $x_1 = x_2 = 1/102$ ,  $x_3 = 100/102$ ,  $\sigma_2/\sigma_1 = 0.3$  and  $\sigma_3/\sigma_1 = 0.1$ . Apart from exhibiting a more complicated structure than in the case of binary mixtures—notice, for example, the existence of a negative first maximum for  $B_{11}$  and  $B_{12}$ —again an important difference between our results and those of the PY theory is that we may get positive values for the bridge functions in some regions.

Thus far we have only considered the GHLL prescription for the contact values  $g_{ij}(\sigma_{ij}^+)$  and the isothermal compressibility  $\kappa_T$  derived from the BMCSL equation

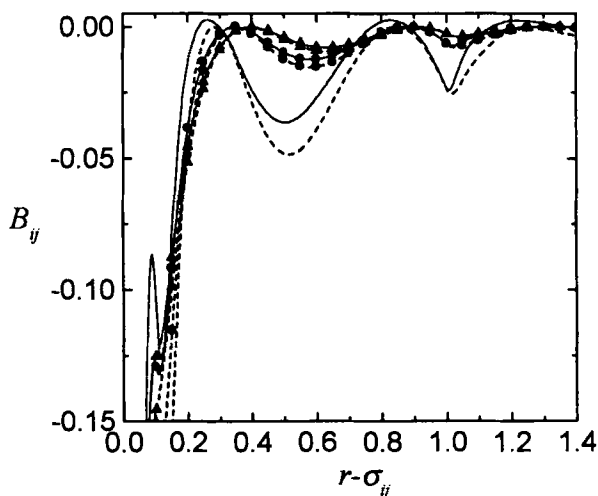


Figure 5. Bridge functions  $B_{ij}(r)$  versus  $r - \sigma_{ij}$  for a ternary mixture of hard spheres with  $\eta = 0.49$ , molar fractions  $x_1 = x_2 = 1/102$  and diameters  $\sigma_3 = 0.1$ ,  $\sigma_2 = 0.3$  and  $\sigma_1 = 1$ . Solid lines: present method; dashed lines: PY results. The curves for  $B_{11}(r)$  contain no symbols, those for  $B_{12}(r)$  contain circles and the ones for  $B_{13}(r)$  contain triangles.

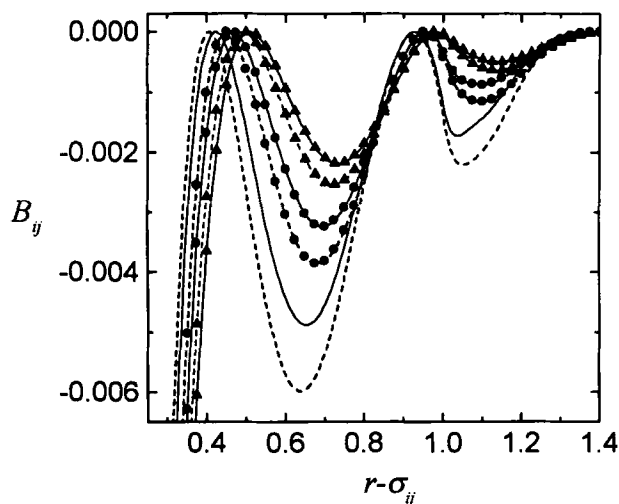


Figure 6. Bridge functions  $B_{ij}(r)$  versus  $r - \sigma_{ij}$  for a ternary mixture of hard spheres with  $\eta = 0.49$ , molar fractions  $x_1 = x_2 = 1/102$ , and diameters  $\sigma_3 = 0.1$ ,  $\sigma_2 = 0.3$  and  $\sigma_1 = 1$ . Solid lines: present method; dashed lines: PY results. The curves for  $B_{22}(r)$  contain no symbols, those for  $B_{23}(r)$  contain circles and the ones for  $B_{33}(r)$  contain triangles.

of state as the input in our method. One may reasonably wonder whether the use of different values for  $g_{ij}(\sigma_{ij}^+)$  and/or  $\kappa_T$  would also yield similar results. In order to assess the importance of other reasonable choices, we have made calculations using the contact values  $g_{ij}(\sigma_{ij}^+)$  obtained by extrapolation of simulation results [18] and the value of  $\kappa_T$  derived from an equation of state for mixtures (eCS) recently proposed by us [26]. To illustrate the results one gets with these choices, in figure 7 we compare the various calculations of the function  $B_{11}(r)$  for the case considered earlier in figure 4, namely the binary mixture defined by  $\eta = 0.49$ ,  $x_1 = 1/16$ ,  $x_2 = 15/16$  and  $\sigma_2/\sigma_1 = 0.3$ . Except in the region up to the first maximum and near the second minimum, the curves obtained with either the BMCSL equation of state and with the second choice (eCS) using our procedure are practically indistinguishable. Nevertheless, although the first maximum with the eCS choice is still positive, its amplitude is much smaller than the one using the BMCSL equation of state, up to a point where the positive character can hardly be ascertained on the scale of the figure. It is also worth pointing out that the value of  $\alpha$  is more sensitive to the choice of  $\kappa_T$  than to the values of  $g_{ij}(\sigma_{ij}^+)$ . In fact, for this mixture one gets  $\alpha = 0.0189$  using the BMCSL equation of state while  $\alpha = 0.0118$  using our proposal (eCS) for the equation of state. A smaller value of  $\alpha$  means that  $c_{11}(r)$  goes to zero more rapidly which in turn implies a much smaller (but still positive) value for the first maximum of  $B_{11}(r)$  in the latter case.

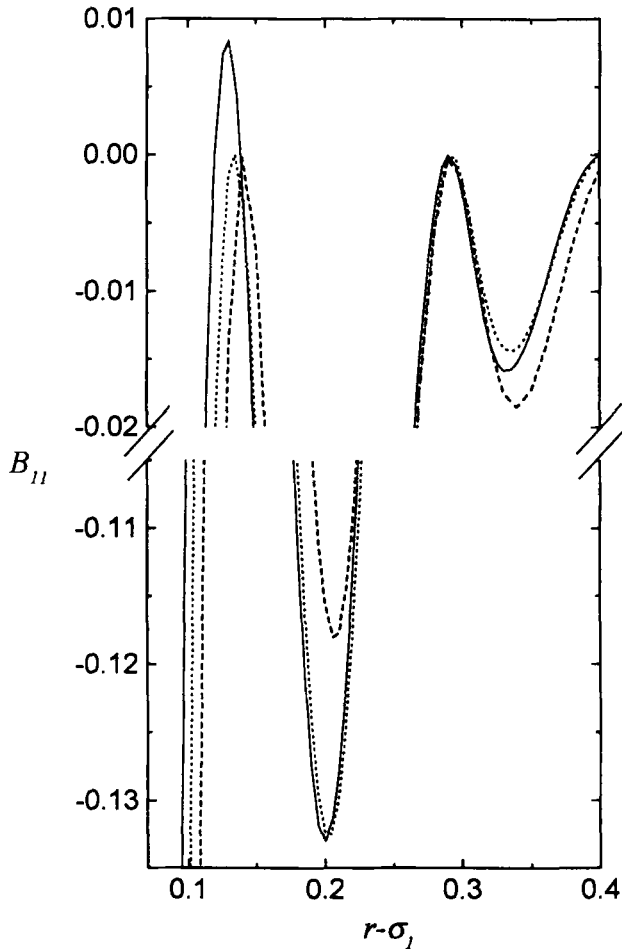


Figure 7. Bridge function  $B_{11}(r)$  versus  $r - \sigma_1$  for a binary mixture of hard spheres with  $\eta = 0.49$ , molar fraction  $x_1 = 1/16$  and diameters  $\sigma_2 = 0.3$  and  $\sigma_1 = 1$ . Solid line: present method using the GHLL contact values of  $g_{ij}(\sigma_{ij}^+)$  and the compressibility  $\kappa_T$  derived from the BMCSL equation of state; dotted line: present method using the contact values of  $g_{ij}(\sigma_{ij}^+)$  obtained by extrapolation of the simulation data in [18] (namely,  $g_{11} = 10.23$ ,  $g_{12} = 4.69$  and  $g_{22} = 3.57$ ) and the compressibility  $\kappa_T$  derived from the equation of state eCS proposed in [26]; dashed line: PY results.

#### 4. Discussion

The points arising from the results of the previous sections deserve further elaboration. To begin with, it is fair to say that our approach leads to a simple and clearcut procedure for determining both the bridge functions and the direct correlation functions in a multicomponent hard-sphere mixture, requiring as the *only input* the contact values of the radial distribution functions that specify the actual equation of state of the mixture. It should be pointed out that while the procedure is capable of yielding the values of the direct correlation functions for all distances, including those inside the hard cores, in the case of the bridge functions it is lim-

ited to distances greater than the contact distance. This is due to the fact that our method does not deal neither with closures nor with the cavity functions. Nevertheless, this restriction may be disposed of, at least for the case of the pure hard-sphere fluid, by considering approximate analytical forms of the cavity function that are available in the literature [8, 24, 27]. In this connection, we should mention that the form of the cavity function derived by Zhou and Stell [8] has been shown to be compatible with our  $g(r)$  in the sense that it yields the same values for both  $g(\sigma^+)$  and  $dg(r)/dr|_{r=\sigma^+}$  [28]. If the available simulation results for the radial distribution functions for mixtures are scarce, those for the bridge functions are to our knowledge non-existent. In the absence of such data to compare with the results we have presented, it would be of course premature to reach definite conclusions. One could argue that the accuracy of the bridge functions might be estimated indirectly by comparing the radial distribution functions calculated using the OZ equation with a given closure and simulation results. In the present approach, however, this is unnecessary since we have explicit (analytical) expressions for the radial distribution functions from the very beginning, and these have already been compared to simulation results both for the one-component and two-component hard-sphere systems in [20, 21].

It is clear that a key difference between our results for the bridge functions and most of those previously reported, is the fact that in our case these functions may attain both *positive and negative* values. In connection with this issue one cannot overlook the fact that it has often been assumed that the bridge functions should be non-positive. This is certainly the case in the PY theory and various parametrizations and approximations have included such an assumption. Nevertheless, as Rast *et al.* [11] have recently pointed out, there seems to be no rigorous reason or argument stating that it should be so. In fact, any theory that leads to a positive value of the direct correlation function  $c(r)$  at a distance where  $g(r) = 1$  will produce a positive  $B(r)$  at that distance. For instance, taking the Monte Carlo data for  $c(r)$  obtained by Groot *et al.* [29] and those of  $g(r)$  given by Barker and Henderson [30], one finds that  $B(r) \simeq 0.2$  for  $r \simeq 1.85\sigma$  and  $\eta = 0.445$ . In further support of the likely correctness of our results, one can invoke the fact that in our case thermodynamic consistency is an ingredient of the formulation while for instance the PY theory does not share this property. For the pure hard-sphere fluid, the reasonable compatibility between our bridge function and the one computed using in particular the RY closure (which was originally proposed to achieve thermodynamic consistency) is very satisfactory in this respect. Further, the

fact that our  $g_{ij}(r)$  are in better agreement with simulation results than those of the PY theory, particularly in the region around the contact point [21], also favours the present approach.

Concerning the ML parametrization for mixtures and the apparent regularity of the shifted bridge functions that was conjectured to hold in general in [19], we can only add that unfortunately it does not do so. Indeed, it would have been rather remarkable that the relatively simple forms proposed for the bridge functions would have been able to capture the rich and varied behaviours that one would expect from the number of parameters involved in the description of mixtures.

Finally, we want to point out that due to the similarity of the bridge functions corresponding to different potentials and those of hard-spheres [15]—in fact the *universality* of the hard-sphere bridge functional has been recently shown to be very reliable [10]—these results are not only relevant for hard-sphere mixtures, but they may also prove useful in connection with the integral equation approach in liquid theory for mixtures with other interaction potentials.

Fruitful discussions with F. del Río, who suggested this problem to us, are gratefully acknowledged. One of us (MLH) wants to thank the Universidad de Extremadura at Badajoz, where the draft of the paper was prepared, for its hospitality. He also acknowledges the partial support of DGAPA-UNAM under Project IN-117798. The work of two of us (SBY and AS) has been partially supported by DGES (Spain) through grant No. PB97-1501 and by the Junta de Extremadura-Fondo Social Europeo through grant No. IPR98C019.

### Appendix

From the Fourier transform  $\tilde{c}_{ij}(q)$  one can get the direct correlation function in real space as

$$c_{ij}(r) = \frac{1}{(2\pi)^3} \int d\mathbf{q} \exp(-i\mathbf{q}\cdot\mathbf{r}) \tilde{c}_{ij}(q) \quad (\text{A } 1)$$

$$= \frac{1}{4\pi^2 i r} \int_{-\infty}^{\infty} dq q \exp(iqr) \tilde{c}_{ij}(q). \quad (\text{A } 2)$$

It is now convenient to see  $q$  as a complex variable. Thus, if  $r > \sigma_{ij}$ , it is possible to take a contour integration around the upper half plane in equation (A1). According to equation (10), the functions  $\tilde{c}_{ij}(q)$  have a *common* set of poles, namely the zeros of  $D(q) \equiv \det[\mathbf{I} + \hat{\mathbf{H}}(q)]$ . A careful inspection of the results obtained from our method shows that the zeros of  $D(q)$  are the roots of a polynomial in  $q^2$  of degree  $N$ . More specifically, the zeros of  $D(q)$  are  $q = \pm i z_{\ell}$ , where the  $z_{\ell}$  ( $\ell = 1, \dots, N$ ) are positive real numbers.

Application of the residue theorem yields

$$c_{ij}(r) = \frac{i}{2\pi r} \sum_{\ell=1}^N z_{\ell} \exp(-z_{\ell} r) \lim_{q \rightarrow i z_{\ell}} \tilde{c}_{ij}(q) (q - i z_{\ell}), \quad r > \sigma_{ij}, \quad (\text{A } 2)$$

which is equivalent to equations (11) and (12). To be more explicit, let us rewrite equation (10) as

$$\hat{\mathbf{C}}(q) = \mathbf{I} - \mathbf{F}^{-1}(q), \quad (\text{A } 3)$$

where  $\mathbf{F}(q) \equiv \mathbf{I} + \hat{\mathbf{H}}(q)$ . Therefore, equation (13) is equivalent to

$$K_{ij}^{(\ell)} = - \frac{\exp(-z_{\ell} \sigma_{ij})}{4\pi(\rho_i \rho_j)^{1/2}} \lim_{q \rightarrow i z_{\ell}} [\mathbf{F}^{-1}(q)]_{ij} (q^2 + z_{\ell}^2). \quad (\text{A } 4)$$

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