Structure of multi-component hard-sphere mixtures

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A method to obtain (approximate) analytical expressions for the radial distribution functions and structure factors in a multi-component mixture of additive hard spheres is introduced. In this method, only contact values of the radial distribution function and the isothermal compressibility are required and thermodynamic consistency is achieved. The approach is simpler than but yields equivalent results to the Generalized Mean Spherical Approximation. Calculations are presented for a binary and a ternary mixture at high density in which the Boublík-Mansoori-Carnahan-Starling-Leland equation of state is used. The results are compared with the Percus-Yevick approximation and the most recent simulation data. © *1998 American Institute of Physics.* [S0021-9606(98)51209-3]

I. INTRODUCTION

Modern liquid state theory relies heavily on the knowledge and understanding of the thermodynamic and structural properties of model systems. Among these, the hard-sphere system has been studied intensively for two main reasons. On the one hand, the hard-sphere potential accounts rather well for the high density and temperature region of the fluid phase diagram of real fluids. This is due to the fact that in this region the fluid structure is dominated by packing effects determined by the short-range repulsive interactions. On the other hand, it allows one to derive (reasonably accurate) analytical expressions for the thermodynamic and structural properties which in turn serve as the basis for the application of perturbation theories in which the hard-sphere fluid is the reference system.[1,2]

The statistical mechanical study of hard-sphere fluid mixtures had a prime time in the 60's and early 70's,[3–12] after which it received much less attention for many years. Both the thermodynamic and the structural properties are related to the radial distribution functions $g_{ij}(r)$ (where i and j label the species and r is the distance) or, equivalently in Fourier space, to the (static) structure factors $S_{ij}(q)$ (where q is the wave number). Therefore, various theories and computer simulations have been devoted to obtain such quantities. Most of the studies have concentrated on binary additive mixtures, although ternary mixtures[13] and non-additive ones[14] have also been considered recently. Computer simulations are harder to perform in mixtures than in pure hard-sphere fluids so it is no surprise that the available simulation data are rather scarce for mixtures, although the recent renewed interest in these systems[15–17] promises to reverse the trend. Undoubtedly, the exact solution of the Percus-Yevick (PY) equation for a multi-component additive mixture by Lebowitz[3] and the subsequent study of the thermodynamic properties of a binary mixture by Lebowitz and Rowlinson[4] played a prominent role in promoting the early developments. This exact solution provides explicit expressions for the Laplace transforms of $rg_{ij}(r)$, in terms of the number densities $\{\rho_i\}$ and the diameters $\{\sigma_i\}$. As mentioned above, from the knowledge of $g_{ij}(r)$ one can immediately obtain the thermodynamic properties. For example, the equation of state for an N-component hard-sphere mixture is given by

$$\frac{p}{\rho k_B T}=1+\frac{2}{3}\pi\rho\sum_{i=1}^{N}\sum_{j=1}^{N}x_i x_j\sigma_{ij}^3 g_{ij}(\sigma_{ij}), \tag{1.1}$$

where p is the pressure, k_B is the Boltzmann constant, T is the temperature, $\rho=\Sigma_i\rho_i$ is the total number density, $x_i=\rho_i/\rho$ is the molar fraction of species i, and $\sigma_{ij}\equiv\frac{1}{2}(\sigma_i+\sigma_j)$. Another usual route to the thermodynamic properties is through the isothermal susceptibility χ (or, equivalently, the isothermal compressibility $\kappa_T=\chi/\rho k_B T$):

$$\chi^{-1}=\frac{1}{k_B T}\left(\frac{\partial p}{\partial\rho}\right)_T=\frac{1}{k_B T}\sum_{i=1}^{N}x_i\left(\frac{\partial p}{\partial\rho_i}\right)_T$$
$$=1-\rho\sum_{i=1}^{N}\sum_{j=1}^{N}x_i x_j\tilde{c}_{ij}(0), \tag{1.2}$$

where $\tilde{c}_{ij}(q)$ is the Fourier transform of the direct correlation function, which is defined by the Ornstein-Zernike equation

$$\tilde{h}_{ij}(q)=\tilde{c}_{ij}(q)+\sum_{k=1}^{N}\rho_k\tilde{h}_{ik}(q)\tilde{c}_{kj}(q), \tag{1.3}$$

with

$$\tilde{h}_{ij}(q)=\int d\mathbf{r}e^{-i\mathbf{q}\cdot\mathbf{r}}h_{ij}(r), \tag{1.4}$$

where $h_{ij}(r)\equiv g_{ij}(r)-1$. As in the one-component case, it turns out that in the PY approximation the pressure derived

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from Eq. (1.1) and the isothermal susceptibility derived from Eq. (1.2) are not thermodynamically consistent. Since both routes to the equation of state are in reasonable agreement with simulation data, in the same spirit as for the single component system, Boublík[9] and, independently, Mansoori *et al.*[10] proposed an equation of state (BMCSL) that interpolates between the two PY results, namely

$$\frac{p}{k_BT}=\frac{\rho}{1-\eta}+\frac{\pi}{2}\frac{\zeta_1\zeta_2}{(1-\eta)^2}+\frac{\pi^2}{36}\zeta_2^3\frac{3-\eta}{(1-\eta)^3}, \tag{1.5}$$

where $\zeta_n\equiv\Sigma_i\rho_i\sigma_i^n$ and $\eta=(\pi/6)\,\zeta_3$ is the volume packing fraction. The isothermal susceptibility that follows from this equation of state (to be used below) is

$$\chi=\rho\left[\frac{\rho}{(1-\eta)^2}+\pi\frac{\zeta_1\zeta_2}{(1-\eta)^3}+\frac{\pi^2}{36}\zeta_2^3\frac{9-4\eta+\eta^2}{(1-\eta)^4}\right]^{-1}. \tag{1.6}$$

Notice that the knowledge of the pressure does not suffice to get $g_{ij}(\sigma_{ij})$ from Eq. (1.1) in a unique way. This problem was addressed by Grundke and Henderson[11] and Lee and Levesque,[12] who proposed an interpolation between the $g_{ij}(\sigma_{ij})$ of the PY solution and the ones arising in the scaled particle theory.[5] This GHLL expression (also to be used later on) is

$$g_{ij}(\sigma_{ij})=\frac{1}{2\pi}\left(\lambda+\frac{1}{2}\lambda'\frac{\sigma_i\sigma_j}{\sigma_{ij}}+\frac{1}{18}\frac{\lambda'^2}{\lambda}\frac{\sigma_i^2\sigma_j^2}{\sigma_{ij}^2}\right), \tag{1.7}$$

where $\lambda\equiv 2\pi/(1-\eta)$ and $\lambda'\equiv\pi^2\zeta_2/(1-\eta)^2$. An interesting aspect of the GHLL proposal is that, upon substitution of Eq. (1.7) into Eq. (1.1), one gets the BMCSL equation of state.

The first authors to publish computer simulation data for the radial distribution functions of a hard-sphere mixture were Lee and Levesque.[12] Their main concern was the application of perturbation theory in fluid mixtures taking hard spheres as the reference system. For many years these simulation data served as the most important source for assessing the merits of theoretical results obtained from the solution of the Ornstein-Zernike equation with different closures or from other approaches. One of the outcomes of the simulations was to show both the merits and the limitations of the PY predictions. This prompted new efforts to improve those predictions without at the same time increasing excessively the complexity of the theory. Among these efforts, it is worth to mention the early generalization to the case of mixtures[11,12] of the Verlet-Weis parameterization.[18] At a more fundamental level, Blum and Høye[19] solved the Generalized Mean Spherical Approximation (GMSA) for mixtures. This approximation consists of solving the Ornstein-Zernike equation, Eq. (1.3), with the Yukawa closure $c_{ij}(r)=K_{ij}e^{-z(r-\sigma_{ij})}/r$ for $r>\sigma_{ij}$. This is a generalization of the PY closure, to which it reduces if $K_{ij}=0$ and/or $z\to\infty$. For the true Yukawa closure, the parameters K_{ij} and z can be determined from given values of $g_{ij}(\sigma_{ij})$ and χ, which demands in general heavy algebraic and numerical labor.[20] In fact, a simplified version of the GMSA has been recently proposed.[21] The results indicate that the GMSA corrects the PY performance and it is comparable to and, in some cases, even better than the generalized Verlet-Weis parameterization. On another vein but with the same aim, Boublík[22] has very recently presented simple expressions for the radial distribution functions for multi-component mixtures, based essentially on geometrical arguments. However, in contrast with what already occurs with the PY approximation, it seems that Boublík's expressions are unable to capture the richness of the behavior found by Malijevský *et al.*[17] in computer simulations of binary mixtures with disparate diameters and at low concentrations of the largest component.

In previous work[23,24] we developed a rational function approximation (RFA) method to find analytical expressions for the radial distribution function of a pure hard-sphere fluid. The same approach was used in a one-component sticky-hard-sphere fluid[25] as well as for the square-well fluid.[26] It is the major purpose of this paper to carry out an extension of the RFA method to the case of multi-component hard-sphere mixtures. As discussed below, this extension will prove to give equivalent results to the GMSA requiring much less effort.

The organization of the paper is as follows. In Sec. II we describe the RFA method for the pure hard-sphere fluid. This does not only make this work self-contained, but also allows us to present the method in a version that is more amenable for direct generalization. Section III deals with the generalization of the RFA approach to the case of an N-component hard-sphere additive mixture. Explicit expressions are provided for the Laplace transforms of $rg_{ij}(r)$ and for the structure factors $S_{ij}(q)$ in terms of the number densities and the diameters of the spheres of each species. Some mathematical details are relegated to two appendices. The method requires as input the contact values $g_{ij}(\sigma_{ij})$ and the isothermal susceptibility χ, for which in Sec. IV we adopt the GHLL and BMCSL prescriptions, respectively, to illustrate its use in the particular cases of a binary and a ternary mixture. The results of our approach are also compared there with those of the PY approximation and with those available from computer simulations. The paper is closed in Sec. V with further discussion and some concluding remarks.

II. THE SINGLE COMPONENT CASE

In this section we give an outline of the RFA method for a one-component hard-sphere fluid, i.e. for the case $N=1$ or, alternatively, $\sigma_i=\sigma$. This presentation, which is equivalent to the one given in Refs. 23 and 24, where all details can be found, is more suitable than the former for direct generalization to the case of mixtures. The starting point will be the Laplace transform

$$G(s)=\int_0^\infty dr e^{-sr}rg(r) \tag{2.1}$$

and the auxiliary function $\Psi(s)$ defined through

$$G(s)=\frac{s}{2\pi}[\rho+e^{s\sigma}\Psi(s)]^{-1}. \tag{2.2}$$

Since $g(r)=0$ for $r<\sigma$ while $g(r)=$finite for $r>\sigma$, one must have that $\lim_{s\to\infty}se^{s\sigma}G(s)=$finite or, equivalently,

$$\lim_{s\to\infty} s^{-2}\Psi(s) = \text{finite}. \tag{2.3}$$

On the other hand, the isothermal compressibility is also finite, so that $\lim_{s\to 0}[G(s)-s^{-2}]=$ finite; this in turn implies

$$\Psi(s) = -\rho+\rho\sigma s-\frac{1}{2}\rho\sigma^2 s^2+\left(\frac{1}{6}\rho\sigma^3+\frac{1}{2\pi}\right)s^3 - \left(\frac{1}{24}\rho\sigma^3+\frac{1}{2\pi}\right)\sigma s^4+\mathscr{O}(s^5). \tag{2.4}$$

An interesting aspect to be remarked is that the minimal input we have just described on the physical requirements related to the structure and thermodynamics of the system is enough to determine the small and large s limits of $\Psi(s)$. While infinite choices for $\Psi(s)$ would comply with such limits, a particularly simple form is a rational function. In particular, the simplest one is

$$\Psi(s) = \frac{S^{(0)}+S^{(1)}s+S^{(2)}s^2+S^{(3)}s^3}{L^{(0)}+L^{(1)}s}, \tag{2.5}$$

where one of the coefficients can be given an arbitrary nonzero value. We choose $S^{(3)}=1$. With such a choice and in view of Eq. (2.4), one finds $S^{(0)}=-\rho L^{(0)}$, $S^{(1)}=-\rho(L^{(1)}-\sigma L^{(0)})$, $S^{(2)}=\rho(\sigma L^{(1)}-\frac{1}{2}\sigma^2 L^{(0)})$, and

$$L^{(0)} = 2\pi\frac{1+2\eta}{(1-\eta)^2}, \tag{2.6}$$

$$L^{(1)} = 2\pi\sigma\frac{1+\frac{1}{2}\eta}{(1-\eta)^2}. \tag{2.7}$$

Upon substitution of these results into Eqs. (2.2) and (2.5), we get

$$G(s) = \frac{e^{-\sigma s}}{2\pi s^2}\frac{L^{(0)}+L^{(1)}s}{1-\rho[\varphi_2(\sigma s)\sigma^3 L^{(0)}+\varphi_1(\sigma s)\sigma^2 L^{(1)}]}, \tag{2.8}$$

where

$$\varphi_n(x)\equiv x^{-(n+1)}\left(\sum_{m=0}^{n}\frac{(-x)^m}{m!}-e^{-x}\right). \tag{2.9}$$

Notice that Eq. (2.8) coincides with the solution to the PY closure of the Ornstein-Zernike equation.[2]

In the spirit of the RFA, the simplest extension of Eq. (2.5) involves two new terms, namely $S^{(4)}s^4$ in the numerator and $L^{(2)}s^2$ in the denominator, both of them necessary in order to satisfy Eq. (2.3). Such an addition leads to

$$G(s) = \frac{e^{-\sigma s}}{2\pi s^2}\frac{L^{(0)}+L^{(1)}s+L^{(2)}s^2}{1+\alpha s-\rho[\varphi_2(\sigma s)\sigma^3 L^{(0)}+\varphi_1(\sigma s)\sigma^2 L^{(1)}+\varphi_0(\sigma s)\sigma L^{(2)}]}, \tag{2.10}$$

where we have identified $S^{(4)}\equiv\alpha$ and now

$$L^{(0)} = 2\pi\frac{1+2\eta}{(1-\eta)^2}+\frac{12\eta}{1-\eta}\left(\frac{\pi}{1-\eta}\frac{\alpha}{\sigma}-\frac{L^{(2)}}{\sigma^2}\right), \tag{2.11}$$

$$L^{(1)} = 2\pi\sigma\frac{1+\frac{1}{2}\eta}{(1-\eta)^2}+\frac{2}{1-\eta}\left(\pi\frac{1+2\eta}{1-\eta}\alpha-3\eta\frac{L^{(2)}}{\sigma}\right). \tag{2.12}$$

Thus far, irrespective of the values of the coefficients $L^{(2)}$ and α, the conditions $\lim_{s\to\infty} s e^{s\sigma}G(s)=$ finite and $\lim_{s\to 0}[G(s)-s^{-2}]=$ finite are satisfied. Of course, if $L^{(2)}=\alpha=0$, one recovers the PY approximation. More generally, we may determine these coefficients by prescribing given values for the contact value $g(\sigma)$ and the isothermal susceptibility χ. This leads to

$$g(\sigma) = \frac{L^{(2)}}{2\pi\alpha\sigma}, \tag{2.13}$$

$$\chi = \left(\frac{2\pi}{L^{(0)}}\right)^2\left[1-\frac{12\eta}{1-\eta}\frac{\alpha}{\sigma}\left(1+2\frac{\alpha}{\sigma}\right)+\frac{12\eta}{\pi}\frac{\alpha L^{(2)}}{\sigma^3}\right]. \tag{2.14}$$

Clearly, upon substitution of Eqs. (2.11) and (2.13) into Eq. (2.14) a quadratic algebraic equation for α is obtained. The physical root is the one that ensures that $L^{(0)}/L^{(2)}>0$ and it turns out to be the smallest root. It is worthwhile to point out that the structure implied by Eq. (2.10) coincides in this one-component case with the solution of the GMSA.[27]

III. THE MULTI-COMPONENT CASE

The method outlined in the previous Section will be now extended to an N-component mixture. First, we introduce the Laplace transforms of $rg_{ij}(r)$:

$$G_{ij} = \int_0^\infty dr e^{-sr} r g_{ij}(r). \tag{3.1}$$

We note that

$$g_{ij}(r) = \Theta(r-\sigma_{ij})[g_{ij}(\sigma_{ij})+g'_{ij}(\sigma_{ij})(r-\sigma_{ij})+\cdots], \tag{3.2}$$

where $\Theta(x)$ is the Heaviside step function and $g'_{ij}(r)\equiv dg_{ij}(r)/dr$. This property imposes a constraint on the large s behavior of $G_{ij}(s)$, namely

$$s e^{\sigma_{ij}s}G_{ij}(s) = \sigma_{ij}g_{ij}(\sigma_{ij})+[g_{ij}(\sigma_{ij})+\sigma_{ij}g'_{ij}(\sigma_{ij})]s^{-1}+\mathscr{O}(s^{-2}). \tag{3.3}$$

On the other hand, the condition of a finite compressibility implies that $\tilde{h}_{ij}(0)=$ finite. As a consequence, for small s,

$$s^2 G_{ij}(s) = 1+H_{ij}^{(0)}s^2+H_{ij}^{(1)}s^3+\cdots, \tag{3.4}$$

with $H_{ij}^{(0)}, H_{ij}^{(1)}=$ finite and

$$H_{ij}^{(n)} \equiv \int_0^\infty dr(-r)^n r h_{ij}(r). \tag{3.5}$$

We are now in the position to generalize the approximation (2.10) to the N-component case. While such a generalization may be approached in a variety of ways, we have chosen one in which two motivations are apparent. On the one hand, we want to recover the PY result[3] as a particular case in much the same fashion as in the one-component system. On the other hand, we want to maintain the development as simple as possible. Therefore, we propose

$$G_{ij}(s)=\frac{e^{-\sigma_{ij}s}}{2\pi s^2}(\mathsf{L}(s)\cdot[(1+\alpha s)\mathbb{1}-\mathsf{A}(s)]^{-1})_{ij}, \tag{3.6}$$

where $\mathbb{1}$ is the identity matrix and

$$L_{ij}(s)=L_{ij}^{(0)}+L_{ij}^{(1)}s+L_{ij}^{(2)}s^2, \tag{3.7}$$

$$A_{ij}(s)=\rho_i[\varphi_2(\sigma_i s)\sigma_i^3 L_{ij}^{(0)}+\varphi_1(\sigma_i s)\sigma_i^2 L_{ij}^{(1)} + \varphi_0(\sigma_i s)\sigma_i L_{ij}^{(2)}]. \tag{3.8}$$

We note that, by construction, Eq. (3.6) complies with the requirement $\lim_{s\to\infty} s e^{\sigma_{ij}s} G_{ij}(s)=$ finite. Further, in view of Eq. (3.4), the coefficients of s^0 and s in the power series expansion of $s^2 G_{ij}(s)$ must be 1 and 0, respectively. This yields $2N^2$ conditions that allow us to express $\mathsf{L}^{(0)}$ and $\mathsf{L}^{(1)}$ in terms of $\mathsf{L}^{(2)}$ and α. To do so, it is convenient to expand $\mathsf{A}(s)$ in powers of s:

$$\mathsf{A}(s)=\sum_{n=0}^{\infty}\mathsf{A}^{(n)}s^n, \tag{3.9}$$

where

$$A_{ij}^{(n)}=(-1)^n\rho_i\left[\frac{\sigma_i^{n+3}}{(n+3)!}L_{ij}^{(0)}-\frac{\sigma_i^{n+2}}{(n+2)!}L_{ij}^{(1)} + \frac{\sigma_i^{n+1}}{(n+1)!}L_{ij}^{(2)}\right]. \tag{3.10}$$

Substitution of Eq. (3.9) into Eq. (3.6) leads, after simple algebra, to

$$\frac{1}{2\pi}L_{ij}^{(0)}=1-\sum_{k=1}^{N}A_{kj}^{(0)}, \tag{3.11}$$

$$\frac{1}{2\pi}L_{ij}^{(1)}=\alpha+\sigma_{ij}-\sum_{k=1}^{N}A_{kj}^{(1)}-\sum_{k=1}^{N}\sigma_{ik}A_{kj}^{(0)}. \tag{3.12}$$

Equations (3.11) and (3.12) constitute a *linear* set of $2N^2$ equations whose solution is readily obtained. The result is

$$L_{ij}^{(0)}=\lambda+\lambda'\sigma_j+2\lambda'\alpha-\lambda\sum_{k=1}^{N}\rho_k\sigma_k L_{kj}^{(2)}, \tag{3.13}$$

$$L_{ij}^{(1)}=\lambda\sigma_{ij}+\frac{1}{2}\lambda'\sigma_i\sigma_j+(\lambda+\lambda'\sigma_i)\alpha - \frac{1}{2}\lambda\sigma_i\sum_{k=1}^{N}\rho_k\sigma_k L_{kj}^{(2)}, \tag{3.14}$$

where λ and λ' have been defined below Eq. (1.7).

In parallel with the development of the single component case, $\mathsf{L}^{(2)}$ and α can be chosen arbitrarily. Again, the choice $L_{ij}^{(2)}=\alpha=0$ gives the PY solution.[3,28] Since we want to go beyond this approximation, we will determine these coefficients by taking prescribed values for $g_{ij}(\sigma_{ij})$ and χ. In particular, according to Eq. (3.3),

$$g_{ij}(\sigma_{ij})=\frac{L_{ij}^{(2)}}{2\pi\alpha\sigma_{ij}}. \tag{3.15}$$

The condition related to χ is more involved. First, making use of Eq. (3.4), one can get $H_{ij}^{(1)}$ in terms of $\mathsf{L}^{(2)}$ and α. This is done in Appendix A. Also, it is shown there that Eq. (1.2) may be cast into the form

$$\chi^{-1}=\sum_{i=1}^{N}\sum_{j=1}^{N}\sqrt{x_i x_j}[\mathbb{1}+\hat{\mathsf{h}}(0)]_{ij}^{-1}, \tag{3.16}$$

where $\hat{h}_{ij}(0)=-4\pi\sqrt{\rho_i\rho_j}H_{ij}^{(1)}$.

Equations (3.15) and (3.16) are the multi-component analogs of Eqs. (2.13) and (2.14), respectively. In fact, by setting $\sigma_i=\sigma$, all the results of Sec. II are recovered. The final step is achieved after eliminating $L_{ij}^{(2)}$ in favor of α in Eq. (3.15) and substituting into Eq. (3.16). This produces an algebraic equation of degree $2N$,[29] whose physical root is determined by the requirement that $G_{ij}(s)$ is positive definite for positive real s. It turns out that the physical solution corresponds to the smallest real root. Once α is known, upon substitution into Eqs. (3.6), (3.13), (3.14), and (3.15), the scheme is complete. Explicit knowledge of $G_{ij}(s)$ allows us to determine immediately the Fourier transform $\tilde{h}_{ij}(q)$ through the relation

$$\tilde{h}_{ij}(q)=-4\pi\sigma_{ij}^3\,\mathrm{Re}\left.\frac{s^2G_{ij}(s)-1}{s^3}\right|_{s=\mathrm{i}q}. \tag{3.17}$$

The structure factor $S_{ij}(q)$ may be expressed in terms of $\tilde{h}_{ij}(q)$ as[2]

$$S_{ij}(q)=x_i\delta_{ij}+\rho x_i x_j\tilde{h}_{ij}(q). \tag{3.18}$$

In the particular case of a binary mixture, rather than the individual structure factors S_{ij}, it is some combination of them which may be easily associated with fluctuations of the thermodynamic variables.[6,8] Specifically, we introduce for later use the quantities[2]

$$S_{NN}(q)=S_{11}(q)+S_{22}(q)+2S_{12}(q), \tag{3.19}$$

$$S_{Nc}(q)=x_2S_{11}(q)-x_1S_{22}(q)+(x_2-x_1)S_{12}(q), \tag{3.20}$$

and

$$S_{cc}(q)=x_2^2S_{11}(q)+x_1^2S_{22}(q)-2x_1x_2S_{12}(q). \tag{3.21}$$

Also, using Eq. (3.3), one can easily derive the result

$$g'_{ij}(\sigma_{ij})=\frac{1}{2\pi\alpha\sigma_{ij}}\left[L_{ij}^{(1)}-L_{ij}^{(2)}\left(\frac{1}{\alpha}+\frac{1}{\sigma_{ij}}\right)\right], \tag{3.22}$$

which may have some use in connection with perturbation theory.[12] Finally, inverse Laplace transformation of $G_{ij}(s)$ yields $g_{ij}(r)$.[30]

Up to here, the presentation is rather general. In the next section we will apply the method to binary and ternary mixtures. To that end, we will choose $g_{ij}(\sigma_{ij})$ given by the GHLL prescription, Eq. (1.7), and, in order to have thermodynamic consistency, χ will be the one obtained from the BMCSL equation of state, cf. Eq. (1.6). The expressions for $S_{NN}(0)$, $S_{Nc}(0)$ and $S_{cc}(0)$ that follow from the same equation of state in the case of a binary mixture and which will serve to test the thermodynamic consistency of the present approach are derived in Appendix B.

IV. RESULTS

A convenient way of characterizing an N-component hard-sphere mixture is to take the species with the largest diameter as species 1 and to specify the total packing fraction η, the $N-1$ independent molar fractions $x_2, x_3, \ldots, x_N$, and the $N-1$ diameter ratios $\sigma_2/\sigma_1, \sigma_3/\sigma_1, \ldots, \sigma_N/\sigma_1$. In addition, we will take $\sigma_1=1$, which fixes the unit of length. This leads to a $(2N-1)$-dimensional parameter space, whose exhaustive exploration is not feasible, even in the binary case. Therefore, for the sake of illustration, we have chosen one representative example for $N=2$ and another one for $N=3$, both with $\eta=0.49$. The reason for this value of η is two-fold. On the one hand, it corresponds to a rather large density,[31] so that it provides a stringent test of the theory. On the other hand, for binary mixtures it has been widely analyzed both through computer simulations[12,15,17] and approximate theories.[17,20–22,32]

We begin with the binary mixture. In this case, we take $\sigma_2/\sigma_1=0.3$ and $x_2=\frac{15}{16}$, so that $\eta_1\simeq 0.35$ and $\eta_2\simeq 0.14$, where $\eta_i\equiv(\pi/6)\rho_i\sigma_i^3$ is the partial volume fraction of species i. This choice is motivated by the recent and very accurate simulation results by Malijevský *et al.*,[17] in which they find an unusual behavior pattern of the distribution functions at low concentrations of the larger spheres. In Figs. 1–3 we present the radial distribution functions $g_{ij}(r)$ as given by the PY theory, our method, and the simulation results from Ref. 17. The picture that emerges is the following. Both PY and RFA are able to capture the peculiar features observed through the simulations with the latter one exhibiting a slightly overall better performance, especially for g_{11}. The agreement between RFA and simulation is particularly good between contact and the first minimum. Since in this region all the integral equation theories tested in Ref. 17 give poor results (the Martynov-Sarkisov[33] theory being the exception), such an agreement must be regarded as yet another advantage of the RFA approach, apart from its much simpler implementation. This is further confirmed by testing our results against recent comparisons[34,35] of the simulation data for this binary mixture with the generalized Verlet-Weis parameterization[11,12,32] and with an improved integral equation theory (MHNC). The latter theory nevertheless appears to account better for the value at the minimum than the RFA in this instance.

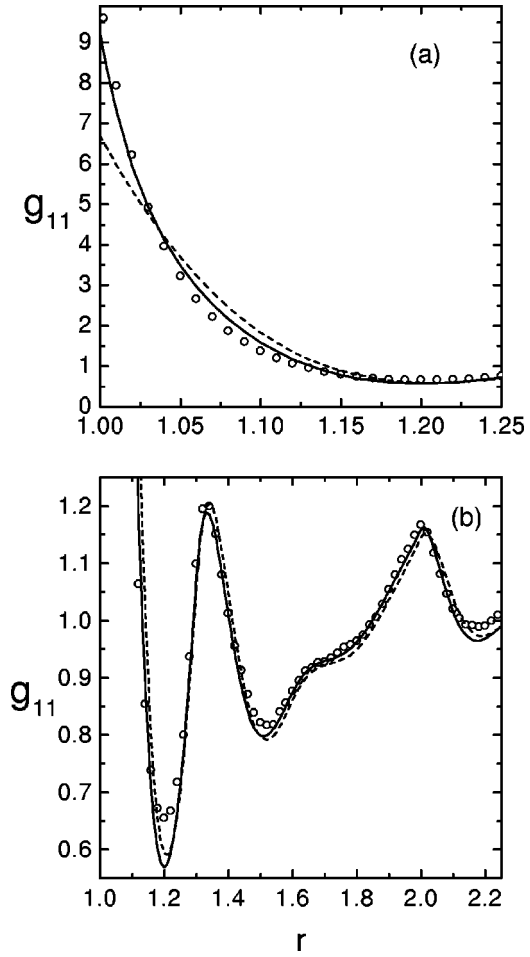

FIG. 1. Comparison of theoretical and simulated values of the radial distribution function $g_{11}(r)$ of the largest spheres as a function of the interparticle distance (in units of σ_1) for the binary mixture $\eta=0.49$, $x_2=\frac{15}{16}$, and $\sigma_2/\sigma_1=0.3$. Points are the simulation values from Ref. 17, the full line represents the RFA results (with $\alpha=0.01886$), and the dashed line corresponds to the PY approximation. (a) Behavior in the vicinity of the contact point. (b) Detailed features of the first few oscillations.

As another illustration of the capabilities of our formulation, in Figs. 4–6 we show the results of $S_{cc}(0)$, $S_{NN}(0)$ and $S_{Nc}(0)$ as functions of the diameter ratio for $\eta=0.49$ and four different molar fractions ($x_2=\frac{1}{4}$, $\frac{1}{2}$, $\frac{3}{4}$, and $\frac{15}{16}$). These results have been derived using two routes. On the one hand, the structural route, through Eqs. (3.17)–(3.21); on the other, the thermodynamic route (cf. Appendix B). The agreement between both routes is practically perfect in the three cases, thus indicating the thermodynamic consistency of our approach.[36] It should be noted that the problem of thermodynamic consistency has been examined by Giunta *et al.*[20] in the context of the GMSA theory. Surprisingly, the three curves displayed in our Fig. 4 corresponding to the cases analyzed in Ref. 20 (cf. their Fig. 6) not only do not show the behavior found there but in fact are totally different. Moreover, since the individual structure factors S_{ij} computed with the RFA are practically indistinguishable from the ones obtained with the GMSA and shown in Figs. 7 and 8 of Ref.

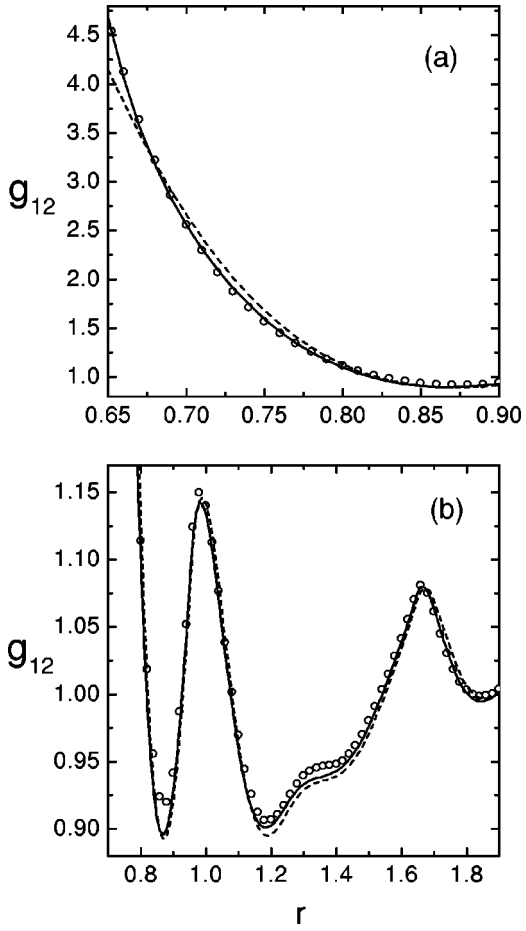

FIG. 2. The same as for Fig. 1 but for g_{12}.

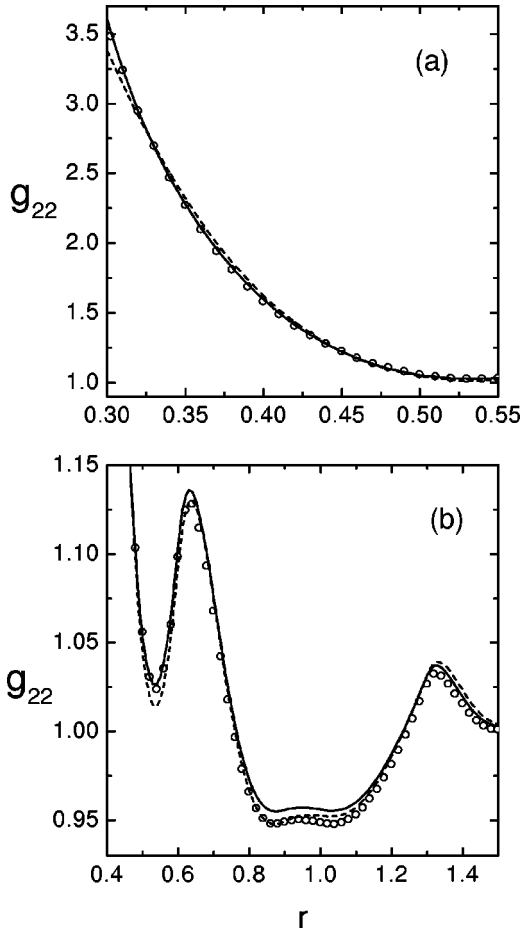

FIG. 3. The same as for Fig. 1 but for g_{22}.

20, we are led to conclude that the results quoted in Figs. 4–6 of the same reference are not correct. Therefore the conclusions drawn from such results are highly questionable. In particular, it seems to us that on the basis of the preceding arguments, the GMSA can indeed be regarded as being thermodynamically self-consistent to a large extent.

We now turn to ternary mixtures for which, unfortunately, no simulation results for the radial distribution functions are to our knowledge available.[37] Here, we have again taken $\eta=0.49$ and $\sigma_2/\sigma_1=0.3$ while now $x_1=x_2=\frac{1}{102}$, $x_3=\frac{100}{102}$ and $\sigma_3/\sigma_1=0.1$. It turns out then that the partial molar fractions are $\eta_1\simeq 0.435$, $\eta_2\simeq 0.012$ and $\eta_3\simeq 0.043$, so that although the particles of species 3 are much smaller than the other particles, they occupy a larger volume than species 2. This case allows us to examine the influence of a third (small) component on the structural properties of the mixture in a situation related to a well studied[12,20,21] binary mixture case in which $\eta=0.49$, $\sigma_2/\sigma_1=0.3$ and $x_1=x_2=\frac{1}{2}$. Figures 7–9 show $g_{11}(r)$, $g_{12}(r)$, and $g_{22}(r)$ obtained from the PY theory and our method. For comparison, we have also included the simulation data[12] as well as our results for the binary mixture mentioned above. Note the excellent agreement between simulation and our approximation also in this binary case; we have observed that this agreement extends to the other two cases considered in Ref. 12. It is also worth pointing out that our numerical values are indistinguishable from those obtained with the GMSA and given in Table I of Ref. 20. Concerning the influence of the third component, it is not only noticeable quantitatively, but it also affects the qualitative features of the radial distribution functions. As expected, $g_{ij}(\sigma_{ij})$, $i,j=1,2$, is in the ternary case larger than in the binary case, due to osmotic depletion effects.[38] How-

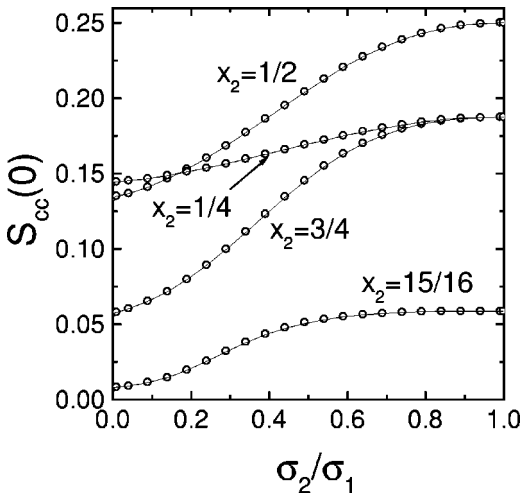

FIG. 4. $S_{cc}(0)$ as a function of σ_2/σ_1 for binary mixtures with $\eta=0.49$ and for four different molar fractions: $x_2=\frac{1}{4}$, $x_2=\frac{1}{2}$, $x_2=\frac{3}{4}$, and $x_2=\frac{15}{16}$. Open circles have been obtained with the RFA structural route, while the continuous line has been derived from the thermodynamic route.

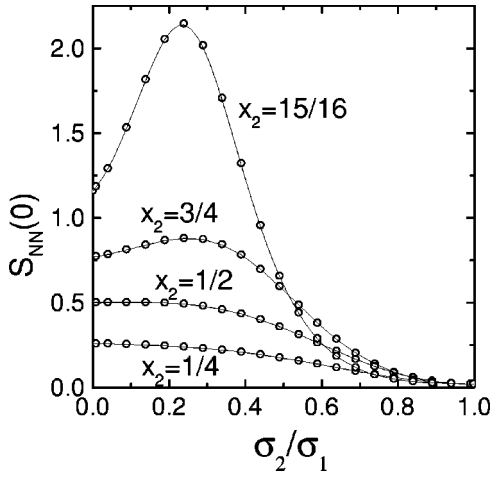

FIG. 5. The same as Fig. 4 but for $S_{NN}(0)$.

ever, the ternary $g_{ij}(r)$ fall off very rapidly, so that they become smaller than their binary counterparts at distances $r \gtrsim \sigma_{ij} + \frac{1}{2}\sigma_3$. In addition, the ternary $g_{ij}(r)$ exhibit a somewhat peculiar behavior at $r \simeq \sigma_{ij} + \sigma_3$, i.e. the distance at which particles of species 3 fit in between particles of species i and j. It is clear that the PY theory captures this peculiarity, although the effect is much less dramatic than in the RFA case. Once again, the most important numerical differences between both approaches show up in the vicinity of the contact points. In Fig. 10 we show $g_{13}(r)$ as an example of the behavior of radial distribution functions involving component 3. In this case (as well as in those of $g_{23}(r)$ and $g_{33}(r)$, not shown here) the differences between PY and RFA are less apparent.

Now we consider the structure factors of the same ternary mixture. Due to the high disparity of diameters and concentrations, the scales of the different functions $S_{ij}(q)$ change very much from one pair to another, cf. Eq. (3.18). For the sake of compactness and without loss of information, we therefore display $\tilde{h}_{ij}(q)/\sigma_{ij}^3$ in Figs. 11 and 12. The effect of the third component is to lower the amplitude of the extrema as compared to that of the binary counterpart, as well as a slight shift of their position. The results of the PY

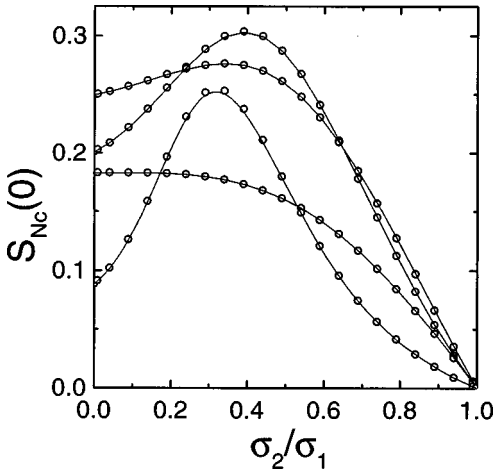

FIG. 6. The same as Fig. 4 but for $S_{Nc}(0)$.

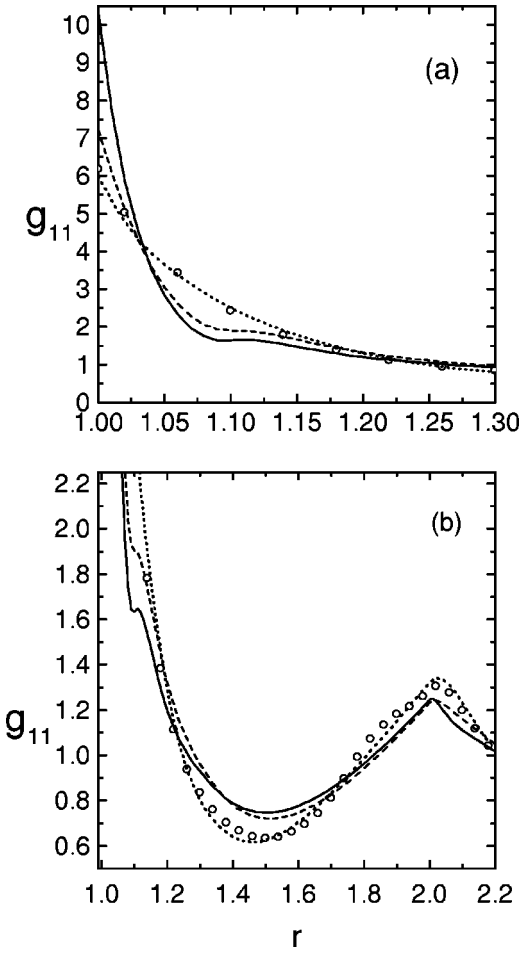

FIG. 7. Comparison of theoretical and simulated values of the radial distribution function $g_{11}(r)$ of the largest spheres as a function of the interparticle distance (in units of σ_1) for the ternary mixture $\eta = 0.49$, $x_1 = x_2 = \frac{1}{102}$, $x_3 = \frac{100}{102}$, $\sigma_2/\sigma_1 = 0.3$, and $\sigma_3/\sigma_1 = 0.1$ and the binary mixture $\eta = 0.49$, $x_1 = x_2 = \frac{1}{2}$, and $\sigma_2/\sigma_1 = 0.3$. Points are the simulation values for the binary mixture from Ref. 12, the dotted line represents the binary RFA results (with $\alpha = 0.02784$), the full line represents the ternary RFA results (with $\alpha = 0.01837$), and the dashed line corresponds to the ternary PY approximation. (a) Behavior in the vicinity of the contact point. (b) Detailed features of the first few oscillations.

approximation differ from those of the RFA method particularly near $q = 0$ and near the first maximum or minimum. In general, Figs. 7–12 confirm the different qualities of $g_{ij}(r)$ and $S_{ij}(q)$ in showing up the structural features of liquids.

V. DISCUSSION

In this paper we have presented a simple extension of the PY approximation for an N-component additive hard-sphere mixture. This extension provides analytical expressions for the radial distribution functions $g_{ij}(r)$ (in Laplace space) and the structure factors $S_{ij}(q)$ in terms of the number densities $\{\rho_i\}$ and the diameters $\{\sigma_i\}$. As input, we require the knowledge of the contact values $g_{ij}(\sigma_{ij})$ and the isothermal susceptibility χ. Clearly, a natural choice is to impose thermodynamic consistency, so that χ readily follows once $g_{ij}(\sigma_{ij})$ have been specified. The formulation involves a single parameter α which obeys an algebraic equation of degree $2N$. In the one-component case, i.e. $N = 1$ or $\sigma_i = \sigma$, our ap-

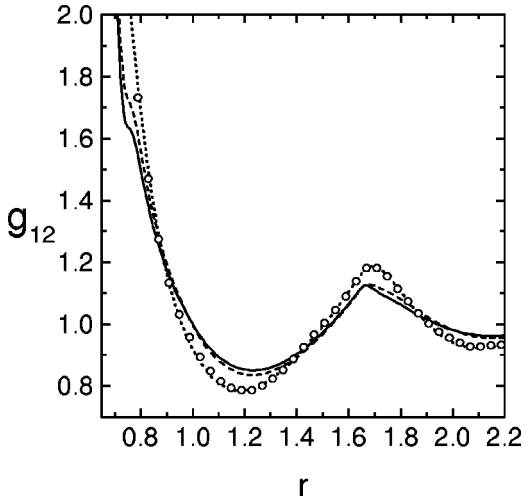

FIG. 8. The same as for case (b) of Fig. 7 but for g_{12}.

proach reduces to the reformulation[23] of the GMSA as a rational function approximation (RFA). In the multicomponent case, however, our scheme, while providing practically identical results, is algebraically much less involved than the GMSA. The latter requires[19] us to deal first with a set of $2N^2$ *nonlinear* equations for given K_{ij} and z and then with another set of $\frac{1}{2}N(N+1)+1$ *nonlinear* equations to obtain K_{ij} and z from the knowledge of $g_{ij}(\sigma_{ij})$ and χ. Already in the binary mixture this yields 12 nonlinear coupled equations[20] and the complexity increases enormously as the number of components grows. In fact, such a complexity has motivated the adoption of simplifying assumptions[21] within the GMSA to produce simple expressions of the Laplace transforms $G_{ij}(s)$. Notwithstanding the merits of this simplification of the GMSA, it is not clear to us whether the removal of one of these assumptions (cf. Eq. (53) in the first paper of Ref. 21), related to the sizes of the spheres and which clearly does not hold for very disparate diameters, would imply the loss of the simplicity. In addition, we note that the simplified version does not reduce to the full GMSA in the case of a one-component fluid.

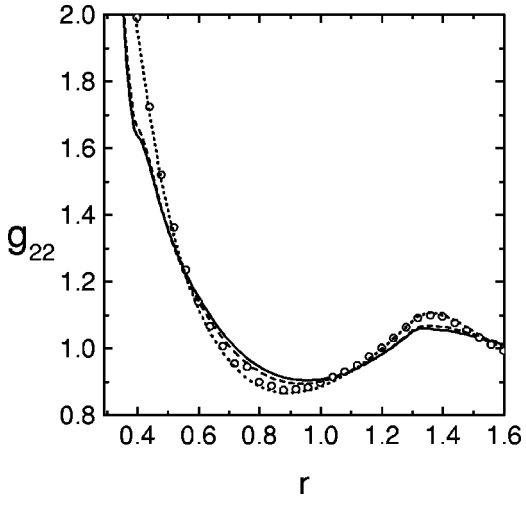

FIG. 9. The same as for case (b) of Fig. 7 but for g_{22}.

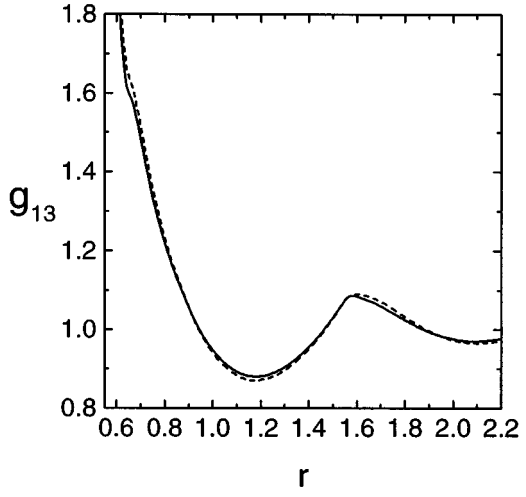

FIG. 10. Detailed features of the first few oscillations of the radial distribution function $g_{13}(r)$, as a function of the interparticle distance (in units of σ_1) for the ternary mixture $\eta=0.49$, $x_1=x_2=\frac{1}{102}$, $x_3=\frac{100}{102}$, $\sigma_2/\sigma_1=0.3$, and $\sigma_3/\sigma_1=0.1$. The full line represents the RFA results (with $\alpha=0.01837$) and the dashed line corresponds to the PY approximation.

The results for the particular binary and ternary mixtures that we chose to illustrate our method were derived by taking $g_{ij}(\sigma_{ij})$ with the GHLL (Refs. 11,12) prescription. This in turn implies that the corresponding equation of state is the BMCSL.[9,10] We found a fairly good agreement with the simulation values, particularly in the vicinity of the contact points, where the PY theory as well as other theories are known[17] to have the worst performance. While a good value at contact is of course ascribable to the equation of state, the better slope at contact and the improvements in the region between contact and the first minimum is certainly an asset of our formulation. The point to be remarked here is that any

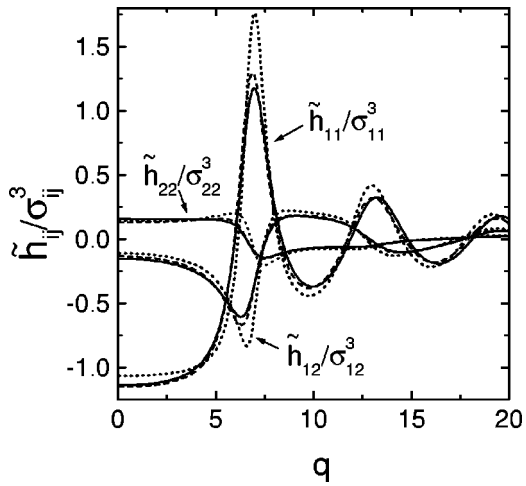

FIG. 11. Fourier transforms $\tilde{h}_{11}(q)$, $\tilde{h}_{12}(q)$, and $\tilde{h}_{22}(q)$ as functions of the wave number q (in units of σ_1^{-1}) for the ternary mixture $\eta=0.49$, $x_1=x_2=\frac{1}{102}$, $x_3=\frac{100}{102}$, $\sigma_2/\sigma_1=0.3$, and $\sigma_3/\sigma_1=0.1$ and the binary mixture $\eta=0.49$, $x_1=x_2=1/2$, and $\sigma_2/\sigma_1=0.3$. The dotted line represents the binary RFA results (with $\alpha=0.02784$), the full line represents the ternary RFA results (with $\alpha=0.01837$), and the dashed line corresponds to the ternary PY approximation.

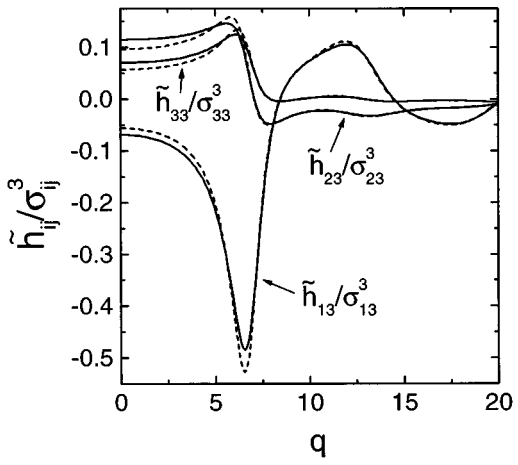

FIG. 12. Fourier transforms $\tilde{h}_{13}(q)$, $\tilde{h}_{23}(q)$, and $\tilde{h}_{33}(q)$ as functions of the wave number q (in units of σ_1^{-1}) for the ternary mixture $\eta=0.49$, $x_1=x_2=\frac{1}{102}$, $x_3=\frac{100}{102}$, $\sigma_2/\sigma_1=0.3$, and $\sigma_3/\sigma_1=0.1$. The full line represents the RFA results (with $\alpha=0.01837$) and the dashed line corresponds to the PY approximation.

accurate equation of state could be equally used instead of the BMCSL.

It is well known that the PY approximation leads to the absence of phase separation into two fluid phases in additive binary hard-sphere mixtures.[4] This was thought to be a genuine feature of the system and not a consequence of the approximation. In fact, the complete miscibility of additive binary mixtures remained unchallenged until quite recently, when Biben and Hansen[39] solved the Ornstein-Zernike equation with the Rogers-Young closure[40] and found that binary mixtures seem to become unstable for sufficiently disparate sizes and at high enough densities. This result has been derived also from a self-consistent density functional theory[41] and supported by experiments on asymmetric colloidal suspensions.[42] Unfortunately, computer simulation is difficult at high densities for mixtures of spheres whose diameters are very different,[43] so this route seems far away at present. Thus, our scheme, not being an integral equation approach, renders itself as another alternative to tackle this problem. In fact, since we are not forced to consider a particular equation of state, it would be interesting to incorporate one that predicts the phase separation of asymmetric binary mixtures,[38,39,41,44] a property absent in the BMCSL equation. A possible candidate might be the equation of state that arises in the work by Lekkerkerker and Stroobants.[44] Nevertheless, such an equation implies the unpleasant feature that, contrary to the experimental evidence,[41] the stable region in the η_1-η_2 plane enlarges as the asymmetry increases.

One aspect that we have also paid attention to is that of the internal consistencies of our approximation. In fact, we have already pointed out the high degree of consistency between the two ways to get $S_{NN}(0)$, $S_{Nc}(0)$, and $S_{cc}(0)$ in the binary mixture, namely the thermodynamic route (cf. Appendix B) and the structural route (cf. Sec. III). Besides, we have checked that $g_{ij}(r)$ is almost indistinguishable from $g_{ji}(r)$ despite the fact that the symmetry requirement was not imposed from the beginning. Of course one can always have strict symmetry by redefining $g_{ij}\to\frac{1}{2}(g_{ij}+g_{ji})$, but this did not prove to be necessary.

Finally, the cases we considered indicate that the differences between the PY theory and the present approach could be more noticeable for ternary mixtures than for binary ones. It is our expectation that this can serve as a motivation for performing more simulations or numerical solutions of integral equations in the case of ternary mixtures.

ACKNOWLEDGMENTS

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APPENDIX A: DERIVATION OF $\mathsf{H}^{(1)}$

Performing a power series expansion of $G_{ij}(s)$, as given by Eq. (3.6), and comparing with Eq. (3.4), one gets

$$\mathsf{H}^{(0)}=\mathsf{B}^{(0)}\cdot(\mathbb{1}-\mathsf{A}^{(0)})^{-1}, \tag{A1}$$

$$\mathsf{H}^{(1)}=\mathsf{B}^{(1)}\cdot(\mathbb{1}-\mathsf{A}^{(0)})^{-1}, \tag{A2}$$

where

$$B_{ij}^{(0)}=\frac{1}{2\pi}L_{ij}^{(2)}+\sum_{k=1}^{N}A_{kj}^{(2)}-\sum_{k=1}^{N}\sigma_{ik}(\alpha\delta_{kj}-A_{kj}^{(1)}) -\sum_{k=1}^{N}\frac{1}{2}\sigma_{ik}^2(\delta_{kj}-A_{kj}^{(0)}), \tag{A3}$$

$$B_{ij}^{(1)}=\sum_{k=1}^{N}A_{kj}^{(3)}+\sum_{k=1}^{N}\sigma_{ik}A_{kj}^{(2)}-\sum_{k=1}^{N}\left(\frac{1}{2}\sigma_{ik}^2+H_{ik}^{(0)}\right)(\alpha\delta_{kj} -A_{kj}^{(1)})-\sum_{k=1}^{N}\left(\frac{1}{6}\sigma_{ik}^3+\sigma_{ik}H_{ik}^{(0)}\right)(\delta_{kj}-A_{kj}^{(0)}). \tag{A4}$$

Equation (A2) gives $\mathsf{H}^{(1)}$ in terms of $\mathsf{L}^{(2)}$ and α. By making use of Eq. (3.15), one can recognize the structure $H_{ij}^{(1)}=P_{ij}(\alpha)/[Q(\alpha)]^2$, where $P_{ij}(\alpha)$ denotes a polynomial in α of degree $2N$ and $Q(\alpha)$ denotes a polynomial of degree N.

In order to express the isothermal compressibility in terms of $\mathsf{H}^{(1)}$, it is convenient to introduce the matrices $\hat{h}_{ij}(q)=\sqrt{\rho_i\rho_j}\tilde{h}_{ij}(q)$ and $\hat{c}_{ij}(q)=\sqrt{\rho_i\rho_j}\tilde{c}_{ij}(q)$. Then the Ornstein-Zernike equation, Eq. (1.3), may be rewritten as $\mathbb{1}-\hat{\mathsf{c}}(q)=[\mathbb{1}+\hat{\mathsf{h}}(q)]^{-1}$. Therefore, Eq. (1.2) becomes

$$\chi^{-1}=\sum_{i=1}^{N}\sum_{j=1}^{N}\sqrt{x_ix_j}[\delta_{ij}-\hat{c}_{ij}(0)] =\sum_{i=1}^{N}\sum_{j=1}^{N}\sqrt{x_ix_j}[\mathbb{1}+\hat{\mathsf{h}}(0)]^{-1}{}_{ij}. \tag{A5}$$

Finally, $\hat{h}_{ij}(0)=-4\pi\sqrt{\rho_i\rho_j}H_{ij}^{(1)}$. It turns out then that, seen as a function of α, χ is the ratio of two polynomials of degree $2N$.

In the binary case, it is straightforward to check that Eq. (A5) is equivalent to

$$\chi=S_{NN}(0)-\frac{S_{Nc}(0)^2}{S_{cc}(0)}=\frac{S_{11}(0)S_{22}(0)-S_{12}^2(0)}{S_{cc}(0)}, \tag{A6}$$

where S_{NN}, S_{Nc}, and S_{cc} are given by Eqs. (3.19)–(3.21).

APPENDIX B: THERMODYNAMIC DERIVATION OF $S_{cc}(0)$, $S_{Nc}(0)$, AND $S_{NN}(0)$ IN A BINARY HARD-SPHERE MIXTURE

The quantities $S_{cc}(0)$, $S_{Nc}(0)$, and $S_{NN}(0)$ measure concentration-concentration, density-concentration, and density-density fluctuations, respectively, in a binary mixture. Their relationships with thermodynamic quantities are[8]

$$S_{cc}(0)=\frac{\mathcal{N}k_BT}{(\partial^2\mathcal{G}/\partial x_1^2)_{p,\mathcal{N},T}}, \tag{B1}$$

$$S_{Nc}(0)=-\delta S_{cc}(0), \tag{B2}$$

$$S_{NN}(0)=\chi+\delta^2 S_{cc}(0), \tag{B3}$$

where $\mathcal{N}$ is the total number of particles, $\mathcal{G}$ is the Gibbs free energy, and

$$\delta\equiv\frac{1}{V}\left(\frac{\partial V}{\partial x_1}\right)_{p,\mathcal{N},T} \tag{B4}$$

is a dilatation factor, V being the volume.

For a general mixture, the Gibbs free energy can be obtained from the knowledge of a given equation of state, i.e. $p/\rho k_BT=Z(\rho,\{x_i\},T)$, as

$$\frac{\mathcal{G}}{\mathcal{N}k_BT}=Z+\frac{\mathcal{A}^{\rm id}+\mathcal{A}^{\rm ex}}{\mathcal{N}k_BT}, \tag{B5}$$

where $\mathcal{A}^{\rm id}$ and $\mathcal{A}^{\rm ex}$ are the ideal and excess contributions to the Helmholtz free energy, respectively. Their expressions are

$$\frac{\mathcal{A}^{\rm id}}{\mathcal{N}k_BT}=-1+\sum_{i=1}^{N}x_i\ln(\rho x_i c_i), \tag{B6}$$

$$\frac{\mathcal{A}^{\rm ex}}{\mathcal{N}k_BT}=\int_0^\rho d\rho'\,\frac{1}{\rho'}[Z(\rho')-1], \tag{B7}$$

where in Eq. (B6) $c_i\equiv h^3/(2\pi m_i k_BT)^{3/2}$, h being the Planck constant and m_i being the mass of a particle of species i.

In Eqs. (B1) and (B4) p rather than ρ plays the role of a state variable, in contrast to what happens in the equation of state. To remedy this problem, consider the mathematical identities

$$\frac{1}{V}\left(\frac{\partial V}{\partial x_1}\right)_p=-\frac{1}{\rho}\frac{(\partial p/\partial x_1)_\rho}{(\partial p/\partial\rho)_{x_1}}, \tag{B8}$$

$$\begin{aligned}\left(\frac{\partial^2\mathcal{G}}{\partial x_1^2}\right)_p=&\left(\frac{\partial^2\mathcal{G}}{\partial x_1^2}\right)_\rho-2\frac{\partial^2\mathcal{G}}{\partial x_1\partial\rho}\frac{(\partial p/\partial x_1)_\rho}{(\partial p/\partial\rho)_{x_1}}\\&+\left(\frac{\partial^2\mathcal{G}}{\partial\rho^2}\right)_{x_1}\left[\frac{(\partial p/\partial x_1)_\rho}{(\partial p/\partial\rho)_{x_1}}\right]^2\\&-\frac{(\partial\mathcal{G}/\partial\rho)_{x_1}}{(\partial p/\partial\rho)_{x_1}}\left\{\left(\frac{\partial^2 p}{\partial x_1^2}\right)_\rho-2\frac{\partial^2 p}{\partial x_1\partial\rho}\frac{(\partial p/\partial x_1)_\rho}{(\partial p/\partial\rho)_{x_1}}\right.\\&\left.+\left(\frac{\partial^2 p}{\partial\rho^2}\right)_{x_1}\left[\frac{(\partial p/\partial x_1)_\rho}{(\partial p/\partial\rho)_{x_1}}\right]^2\right\}\end{aligned} \tag{B9}$$

to find

$$\delta=-\chi\left(\frac{\partial Z}{\partial x_1}\right)_\rho, \tag{B10}$$

$$\frac{1}{\mathcal{N}k_BT}\left(\frac{\partial^2\mathcal{G}}{\partial x_1^2}\right)_p=\frac{1}{x_1x_2}-\chi\left(\frac{\partial Z}{\partial x_1}\right)_\rho^2+\frac{1}{\mathcal{N}k_BT}\left(\frac{\partial^2\mathcal{A}^{\rm ex}}{\partial x_1^2}\right)_\rho, \tag{B11}$$

where we have taken into account the thermoynamic relations $(\partial p/\partial\rho)_{x_1}=k_BT/\chi$, $(\partial\mathcal{G}/\partial\rho)_{x_1}=\mathcal{N}k_BT/\rho\chi$.

In the particular case of a hard-sphere system described by the BMCSL equation of state, Z is given by Eq. (1.5), so that Eq. (B7) yields

$$\begin{aligned}\frac{\mathcal{A}^{\rm ex}}{\mathcal{N}k_BT}=&\left(\frac{\pi^2}{36}\frac{\zeta_2^3}{\rho\eta^2}-1\right)\ln(1-\eta)\\&+\frac{\pi}{36}\zeta_2\frac{18\eta\zeta_1(1-\eta)+\pi\zeta_2^2}{\rho\eta(1-\eta)^2}.\end{aligned} \tag{B12}$$

Furthermore, taking derivatives with respect to x_1 in Eqs. (1.5) and (B12) in the binary case, one gets

$$\begin{aligned}\left(\frac{\partial Z}{\partial x_1}\right)_\rho=&\frac{\pi\zeta_2}{2(1-\eta)^2}(\sigma_1-\sigma_2)+\frac{\pi}{2(1-\eta)^2}(\sigma_1^2-\sigma_2^2)\left[\zeta_1\right.\\&\left.+\frac{\pi\zeta_2^2(3-\eta)}{6(1-\eta)}\right]+\frac{\pi}{6(1-\eta)^2}(\sigma_1^3-\sigma_2^3)\left[\rho\right.\\&\left.+\frac{\pi\zeta_1\zeta_2}{1-\eta}+\frac{\pi^2\zeta_2^3(4-\eta)}{18(1-\eta)^2}\right],\end{aligned} \tag{B13}$$

$$\frac{1}{\mathcal{N}k_BT}\left(\frac{\partial^2\mathcal{A}^{\rm ex}}{\partial x_1^2}\right)_\rho=\frac{\pi\rho}{1-\eta}(\sigma_1-\sigma_2)(\sigma_1^2-\sigma_2^2)+\frac{\pi^2\rho^2}{36(1-\eta)^2}(\sigma_1^3-\sigma_2^3)^2+\frac{\pi^2\rho\zeta_1}{6(1-\eta)^2}(\sigma_1^2-\sigma_2^2)(\sigma_1^3-\sigma_2^3)$$
$$+\frac{\pi^2\rho\zeta_2}{6(1-\eta)^2}(\sigma_1-\sigma_2)(\sigma_1^3-\sigma_2^3)+\frac{\pi^3\rho\zeta_1\zeta_2}{36(1-\eta)^3}(\sigma_1^3-\sigma_2^3)^2+\frac{\pi^2\rho\zeta_2}{6\eta}(\sigma_1^2-\sigma_2^2)^2$$
$$\times\left[\frac{\ln(1-\eta)}{\eta}+\frac{1}{(1-\eta)^2}\right]-\frac{\pi^3\rho\zeta_2^2}{18\eta^2}(\sigma_1^2-\sigma_2^2)(\sigma_1^3-\sigma_2^3)$$
$$\times\left[\frac{\ln(1-\eta)}{\eta}+\frac{\eta^2-5\eta+2}{2(1-\eta)^3}\right]+\frac{\pi^4\rho\zeta_2^3}{216\eta^3}(\sigma_1^3-\sigma_2^3)^2\left[\frac{\ln(1-\eta)}{\eta}-\frac{5\eta^3-26\eta^2+21\eta-6}{6(1-\eta)^4}\right]. \tag{B14}$$

Substitution of Eqs. (1.6), (B13), and (B14) into Eqs. (B10) and (B11) allows one to obtain $S_{cc}(0)$, $S_{Nc}(0)$, and $S_{NN}(0)$ from Eqs. (B1)–(B3), according to the BMCSL equation of state.

[1] T. Boublík, I. Nezbeda, and K. Hlavaty, *Statistical Thermodynamics of Simple Liquids and Their Mixtures* (Elsevier, Amsterdam, 1980); J. S. Rowlinson and F. J. Swinton, *Liquids and Liquid Mixtures*, 3rd ed. (Butterworth, London, 1982).
[2] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids* (Academic, London, 1986).
[3] J. L. Lebowitz, Phys. Rev. **133**, 895 (1964).
[4] J. L. Lebowitz and J. S. Rowlinson, J. Chem. Phys. **41**, 133 (1964).
[5] J. L. Lebowitz, E. Helfand, and E. Praestgaard, J. Chem. Phys. **43**, 774 (1965).
[6] N. W. Ashcroft and D. C. Langreth, Phys. Rev. **156**, 685 (1967).
[7] D. Henderson and J. A. Barker, J. Chem. Phys. **49**, 3377 (1968); R. J. Baxter, *ibid.* **52**, 4559 (1970); J. P. O'Connel, Mol. Phys. **20**, 27 (1971).
[8] A. B. Bathia and D. E. Thornton, Phys. Rev. B **8**, 3004 (1970).
[9] T. Boublík, J. Chem. Phys. **53**, 471 (1970).
[10] G. A. Mansoori, N. F. Carnahan, K. F. Starling, and T. W. Leland, J. Chem. Phys. **54**, 1523 (1971).
[11] E. W. Grundke and D. Henderson, Mol. Phys. **24**, 269 (1972).
[12] L. L. Lee and D. Levesque, Mol. Phys. **26**, 1351 (1973).
[13] D. Gazzillo, Mol. Phys. **83**, 1171 (1994); K. Fotouh and K. Shukla, Chem. Eng. Sci. **51**, 4923 (1996); **51**, 4933 (1996), and references to previous work by Shukla therein.
[14] D. Gazzillo, Mol. Phys. **84**, 303 (1995); J. A. Anta, and G. Kahl, *ibid.* **84**, 1273 (1995); E. Z. Hamad, J. Chem. Phys. **105**, 3222 (1996).
[15] M. Barošová, A. Malijevský, S. Labík, and W. R. Smith, Mol. Phys. **87**, 423 (1996).
[16] D. H. L. Yau, K.-Y. Chan, and D. Henderson, Mol. Phys. **88**, 1237 (1996); E. Z. Hamad, *ibid.* **91**, 371 (1997).
[17] A. Malijevský, M. Barošová, and W. R. Smith, Mol. Phys. **91**, 65 (1997).
[18] L. Verlet and J.-J. Weis, Phys. Rev. A **5**, 939 (1972).
[19] L. Blum and J. S. Høye, J. Stat. Phys. **19**, 317 (1978).
[20] G. Giunta, M. C. Abramo, and C. Caccamo, Mol. Phys. **56**, 319 (1985).
[21] Y. Tang and B. C.-Y. Lu, J. Chem. Phys. **103**, 7463 (1995); Mol. Phys. **84**, 89 (1995).
[22] T. Boublík, Mol. Phys. **91**, 161 (1997).
[23] S. B. Yuste and A. Santos, Phys. Rev. A **43**, 5418 (1991).
[24] S. B. Yuste, M. López de Haro, and A. Santos, Phys. Rev. E **53**, 4820 (1996).
[25] S. B. Yuste and A. Santos, J. Stat. Phys. **72**, 703 (1993); Phys. Rev. E **48**, 4599 (1994).
[26] S. B. Yuste and A. Santos, J. Chem. Phys. **101**, 2355 (1994).
[27] E. Waisman, Mol. Phys. **25**, 45 (1973); D. Henderson and L. Blum,*ibid.* **32**, 1627 (1976); J. S. Høye and L. Blum, J. Stat. Phys. **16**, 399 (1977).
[28] L. Blum and J. S. Høye, J. Phys. Chem. **81**, 1311 (1977).
[29] As a matter of fact, we have not been able to prove this assertion analytically for arbitrary N. However, we have checked it for $N\leqslant 5$.
[30] A code using the MATHEMATICA computer algebra system to obtain $G_{ij}(s)$ and $g_{ij}(r)$ with the present method is available from the web page http://www.unex.es/fisteor/files.html.
[31] In fact, in the case of a one-component hard-sphere fluid, this packing fraction is close to that of the fluid-solid transition, cf. B. J. Alder, W. G. Hoover, and D. A. Young, J. Chem. Phys. **49**, 3688 (1968).
[32] E. Enciso, F. Lado, M. Lombardero, J. L. F. Abascal, and S. Lago, J. Chem. Phys. **87**, 2249 (1987).
[33] G. A. Martynov, *Fundamental Theory of Liquids. Method of Distribution Functions* (Adam Hilger, Bristol, 1992).
[34] E. Enciso (private communication).
[35] C. Caccamo, G. Pellicane, and E. Enciso, Phys. Rev. E **56**, 6954 (1997).
[36] Of course, the consistency is only required for two of these three quantities, since the third one is constrained by the relation (A6).
[37] For *non-additive* ternary mixtures, see H. M. Schaink, Physica A **210**, 113 (1994), where the case $\sigma_{11}=\sigma_{22}=\sigma_{33}=\sigma_{13}=\sigma_{23}=1.25\sigma_{12}$ is considered.
[38] H. Löwen, Physica A **235**, 129 (1997); R. Garibay-Alonso, J. M. Méndez-Alcaraz, and R. Klein, *ibid.* **235**, 159 (1997).
[39] T. Biben and J.-P. Hansen, Phys. Rev. Lett. **66**, 2215 (1991).
[40] F. J. Rogers and D. A. Young, Phys. Rev. A **30**, 999 (1984).
[41] Y. Rosenfeld, Phys. Rev. Lett. **72**, 3831 (1994); J. Phys. Chem. **99**, 2857 (1995); G. Kahl, B. Bildstein, and Y. Rosenfeld, Phys. Rev. E **54**, 5391 (1996).
[42] S. Sanyal, N. Easwar, S. Ramaswamy, and A. K. Sood, Europhys. Lett. **18**, 107 (1992); J. S. van Duijneveldt, A. W. Heinen, and H. N. W. Lekkerkerker, *ibid.* **21**, 369 (1993); P. D. Kaplan, J. L. Rouke, A. Yodh, and D. J. Pine, Phys. Rev. Lett. **72**, 582 (1994).
[43] G. Jackson, J. S. Rowlinson, and F. van Swol, J. Phys. Chem. **91**, 4907 (1987).
[44] H. N. W. Lekkerkerker and A. Stroobants, Physica A **195**, 387 (1993).