Radial distribution functions for a multicomponent system of sticky hard spheres

Andrés Santos[a)] and Santos Bravo Yuste[b)]
Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain

Mariano López de Haro[c)]
Centro de Investigación en Energía, U.N.A.M., Apartado Postal 34, Temixco, Mor. 62580, Mexico

(Received 8 June 1998; accepted 24 July 1998)

A method to obtain (approximate) analytical expressions for the radial distribution functions and structure factors in a multicomponent system of sticky hard spheres is introduced. In its simplest implementation, the method yields the Percus–Yevick approximation. In the next order, only contact values of the cavity functions and the isothermal compressibility are required. Some tentative strategies to determine the input values are discussed. Illustrative examples following these strategies, in which the radial distribution functions and structure factors are computed, are also presented. © *1998 American Institute of Physics.* [S0021-9606(98)52240-4]

I. INTRODUCTION

The knowledge and understanding of the thermodynamic and structural properties of model systems play a key role in the modern developments of liquid state theory.[1] It is unfortunate, however, that very few such models have been amenable to analytical solution and therefore progress has been relatively slow in this area despite a vast amount of literature devoted to the subject. Other than for hard-sphere (HS) systems, the results are rather scarce in the case of pure fluids and the situation is even worse in the case of fluid mixtures. These latter systems pose major difficulties to the use of either computer simulation or integral equation methods, two of the most important tools of liquid state theoreticians.[2] A model which has received a lot of attention recently is the sticky-hard-sphere (SHS) fluid introduced by Baxter in 1968 (Ref. 3) and later extended to multicomponent mixtures by Perram and Smith[4] and independently by Barboy.[5] In this model, the molecular interaction may be defined via square-well potentials of infinite depth and vanishing width. These potentials embody the two essential characteristics of real molecular interactions, namely, a harsh repulsion and an attractive part. In spite of their known shortcomings,[6] an important feature of SHS systems is that they allow for exact solution of the Ornstein–Zernike equation in the Percus–Yevick (PY) approximation.[3,4] Furthermore, they are thought to be appropriate for describing structural properties of colloidal systems, micelles, and microemulsions as well as some aspects of gas–liquid equilibrium, ionic fluids and mixtures, solvent mediated forces, adsorption phenomena, polydisperse systems, and fluids containing chainlike molecules.[7–9]

In previous work[10,11] we developed a rational function approximation (RFA) method to find analytical expressions for the radial distribution function of a pure HS fluid and a multicomponent HS mixture. The same approach was used in a one-component SHS fluid[12,13] as well as for the square-well fluid.[14] It is the major aim of this paper to carry out an extension of the RFA method to the case of a multicomponent mixture of sticky hard spheres. As discussed below, this approach will not only allow us to rederive the results of Perram and Smith[4] in the PY approximation, but also to go beyond such an approximation in what one may refer to as an approach similar to the generalized mean spherical approximation (GMSA) for this system, which to our knowledge has not been derived up to now.

The organization of the paper is as follows. In Sec. II we describe the SHS mixture and give a brief outline of the steps involved in the RFA method. The method requires as input the contact values of the cavity functions, $y_{ij}(\sigma_{ij})$, and the isothermal susceptibility χ. In terms of these quantities, of the number densities and the diameters of the spheres of each species, and of the adhesiveness parameters of each pair, explicit expressions are provided for the Laplace transforms of $rg_{ij}(r)$ and for the structure factors $S_{ij}(q)$. In Sec. III and in the absence of a reliable equation of state and computer simulation results for SHS mixtures, we adopt a particular strategy to illustrate the possible use of our results. In essence, we present two alternative routes to estimate $y_{ij}(\sigma_{ij})$ and χ and compare our approach with the PY approximation. The paper is closed in Sec. IV with further discussion and some concluding remarks.

II. RFA METHOD FOR SHS: DEFINITIONS AND BASIC REQUIREMENTS

Let us consider an N-component mixture of spherical particles with a number density ρ_i of component i. The molar fraction of species i is $x_i=\rho_i/\rho$, where $\rho=\Sigma_{i=1}^{N}\rho_i$ is the total number density, while its diameter is σ_i. Let us also assume that the particles interact according to the square-well potential

[a)]Electronic mail: andres@unexs.es
[b)]Electronic mail: santos@unexs.es
[c)]Electronic mail: malopez@servidor.unam.mx

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$$\varphi_{ij}(r)=\begin{cases}\infty, & r>\sigma_{ij}\\ -\epsilon_{ij}, & \sigma_{ij}<r<R_{ij}\\ 0, & r>R_{ij}.\end{cases} \tag{2.1}$$

Here $\sigma_{ij}=(\sigma_i+\sigma_j)/2$ is the distance between the centers of a sphere of species i and a sphere of species j at contact, ϵ_{ij} is the square-well depth and $R_{ij}-\sigma_{ij}$ indicates the well width. We now take the SHS limit,[3] namely

$$R_{ij}\to\sigma_{ij},\epsilon_{ij}\to\infty,\tau_{ij}\equiv\frac{1}{12}\frac{\sigma_{ij}}{R_{ij}-\sigma_{ij}}e^{-\epsilon_{ij}/k_BT}=\text{finite}, \tag{2.2}$$

where the τ_{ij} are monotonically increasing functions of the temperature T and their inverses measure the degree of ''adhesiveness'' of the interacting spheres i and j. The virial equation of state for the SHS mixture is then given by

$$\begin{aligned}Z\equiv\frac{p}{\rho k_BT}&=1+\frac{1}{6}\rho\sum_{i=1}^{N}\sum_{j=1}^{N}x_ix_j\int d\mathbf{r}ry_{ij}(r)\frac{d}{dr}e^{-\varphi_{ij}(r)/k_BT}\\&=1+\frac{2\pi}{3}\rho\sum_{i=1}^{N}\sum_{j=1}^{N}x_ix_j\sigma_{ij}^3y_{ij}(\sigma_{ij})\\&\quad\times\left[1-\frac{1}{12\tau_{ij}}\left(3+\frac{w_{ij}}{y_{ij}(\sigma_{ij})}\right)\right],\end{aligned} \tag{2.3}$$

where p is the pressure, k_B is the Boltzmann constant, $y_{ij}(r)\equiv g_{ij}(r)e^{\varphi_{ij}(r)/k_BT}$ is the cavity function, $g_{ij}(r)$ being the usual pair distribution function, and $w_{ij}\equiv\lim_{R_{ij}\to\sigma_{ij}}[dy_{ij}(r)/dr]_{\sigma_{ij}^+}$. Since $y_{ij}(r)$ must be continuous, it follows that

$$g_{ij}(r)=y_{ij}(r)\left[\theta(r-\sigma_{ij})+\frac{\sigma_{ij}}{12\tau_{ij}}\delta_+(r-\sigma_{ij})\right]. \tag{2.4}$$

Further, the energy equation of state for this system reads

$$\begin{aligned}u_{\text{ex}}&\equiv\frac{1}{2}\rho\sum_{i=1}^{N}\sum_{j=1}^{N}x_ix_j\int d\mathbf{r}y_{ij}(r)\varphi_{ij}(r)e^{-\varphi_{ij}(r)/k_BT}\\&=-\frac{\pi}{6}\rho\sum_{i=1}^{N}\sum_{j=1}^{N}x_ix_j\epsilon_{ij}\frac{\sigma_{ij}^3}{\tau_{ij}}y_{ij}(\sigma_{ij}),\end{aligned} \tag{2.5}$$

where u_{ex} is the excess internal energy per particle. Another usual route to the thermodynamic properties is through the isothermal susceptibility χ,

$$\begin{aligned}\chi^{-1}&=\frac{1}{k_BT}\frac{\partial p}{\partial\rho}=\frac{1}{k_BT}\sum_{i=1}^{N}x_i\frac{\partial p}{\partial\rho_i}\\&=1-\rho\sum_{i=1}^{N}\sum_{j=1}^{N}x_ix_j\tilde{c}_{ij}(0),\end{aligned} \tag{2.6}$$

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

$$\tilde{h}_{ij}(q)=\tilde{c}_{ij}(q)+\sum_{k=1}^{N}\rho_k\tilde{h}_{ik}(q)\tilde{c}_{kj}(q), \tag{2.7}$$

with

$$\tilde{h}_{ij}(q)=\int d\mathbf{r}e^{-\mathbf{iq}\cdot\mathbf{r}}h_{ij}(r), \tag{2.8}$$

where $h_{ij}(r)\equiv g_{ij}(r)-1$ is the total correlation function.

We are now in a position to carry out the RFA method for the multicomponent SHS mixture. As in previous work,[11] we define the Laplace transform

$$G_{ij}(s)=\int_0^\infty dr\ e^{-sr}rg_{ij}(r). \tag{2.9}$$

The condition $y_{ij}(\sigma_{ij})=\text{finite}$ translates into the following large-s behavior of $G_{ij}(s)$,

$$e^{\sigma_{ij}s}G_{ij}(s)=\sigma_{ij}^2y_{ij}(\sigma_{ij})\left(\frac{1}{12\tau_{ij}}+\sigma_{ij}^{-1}s^{-1}\right)+\mathcal{O}(s^{-2}). \tag{2.10}$$

On the other hand, the condition $\chi^{-1}=\text{finite}$ gives information about the small-s behavior, i.e.,

$$s^2G_{ij}(s)=1+H_{ij}^{(0)}s^2+H_{ij}^{(1)}s^3+\cdots \tag{2.11}$$

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

$$H_{ij}^{(n)}\equiv\int_0^\infty dr(-r)^nrh_{ij}(r). \tag{2.12}$$

The RFA proposal for HS mixtures[11] can be easily extended to the SHS model. In the former case, $e^{\sigma_{ij}s}G_{ij}(s)\sim s^{-1}$ for large s, while now $e^{\sigma_{ij}s}G_{ij}(s)\sim s^0$. Of course, in the special case $\tau_{ij}\to\infty$ one must recover the pure HS case. Consequently, our approximation consists of writing

$$G_{ij}(s)=\frac{e^{-\sigma_{ij}s}}{2\pi s^2}(\mathsf{L}(s)\cdot[(1+\alpha s)\mathbb{1}-\mathsf{A}(s)]^{-1})_{ij}, \tag{2.13}$$

with $\mathbb{1}$ the identity matrix and

$$L_{ij}(s)=L_{ij}^{(0)}+L_{ij}^{(1)}s+L_{ij}^{(2)}s^2+L_{ij}^{(3)}s^3, \tag{2.14}$$

$$\begin{aligned}A_{ij}(s)=\rho_i[&\phi_2(\sigma_is)\sigma_i^3L_{ij}^{(0)}+\phi_1(\sigma_is)\sigma_i^2L_{ij}^{(1)}\\&+\phi_0(\sigma_is)\sigma_iL_{ij}^{(2)}-e^{-\sigma_is}L_{ij}^{(3)}],\end{aligned} \tag{2.15}$$

where

$$\phi_n(x)\equiv x^{-(n+1)}\left(\sum_{m=0}^{n}\frac{(-x)^m}{m!}-e^{-x}\right) \tag{2.16}$$

are the modified incomplete gamma functions. We note that, by construction, Eq. (2.13) complies with the requirement $\lim_{s\to\infty}e^{\sigma_{ij}s}G_{ij}(s)=\text{finite}$. Further, in view of Eq. (2.11), the coefficients of s^0 and s in the power series expansion of $s^2G_{ij}(s)$ 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 $\mathsf{L}^{(2)}$, $\mathsf{L}^{(3)}$, and α. To do so, it is convenient to expand $\mathsf{A}(s)$ as

$$\mathsf{A}(s)=\sum_{n=0}^{\infty}\mathsf{A}^{(n)}s^n, \tag{2.17}$$

where

$$\begin{aligned}A_{ij}^{(n)}=(-1)^n\rho_i\Bigg[&\frac{\sigma_i^{n+3}}{(n+3)!}L_{ij}^{(0)}-\frac{\sigma_i^{n+2}}{(n+2)!}L_{ij}^{(1)}\\&+\frac{\sigma_i^{n+1}}{(n+1)!}L_{ij}^{(2)}-\frac{\sigma_i^n}{n!}L_{ij}^{(3)}\Bigg].\end{aligned} \tag{2.18}$$

Substitution of Eq. (2.17) into Eq. (2.13) leads, after simple algebra, to

$$\frac{1}{2\pi} L_{ij}^{(0)} = 1 - \sum_{k=1}^{N} A_{kj}^{(0)}, \tag{2.19}$$

$$\frac{1}{2\pi} L_{ij}^{(1)} = \alpha + \sigma_{ij} - \sum_{k=1}^{N} A_{kj}^{(1)} - \sum_{k=1}^{N} \sigma_{ik} A_{kj}^{(0)}. \tag{2.20}$$

Equations (2.19) and (2.20) constitute a *linear* set of $2N^2$ equations whose solution is readily obtained. The result is

$$L_{ij}^{(0)} = \lambda + \lambda' \sigma_j + 2\lambda' \alpha - \lambda \sum_{k=1}^{N} \rho_k (\sigma_k L_{kj}^{(2)} - L_{kj}^{(3)}) - \lambda' \sum_{k=1}^{N} \rho_k \sigma_k L_{kj}^{(3)}, \tag{2.21}$$

$$L_{ij}^{(1)} = \lambda \sigma_{ij} + \frac{1}{2} \lambda' \sigma_i \sigma_j + (\lambda + \lambda' \sigma_i) \alpha - \frac{1}{2} \lambda \sigma_i \sum_{k=1}^{N} \rho_k (\sigma_k L_{kj}^{(2)} - L_{kj}^{(3)}) - \frac{1}{2} (\lambda + \lambda' \sigma_i) \sum_{k=1}^{N} \rho_k \sigma_k L_{kj}^{(3)}, \tag{2.22}$$

where $\lambda \equiv 2\pi/(1-\eta)$ and $\lambda' \equiv \pi^2 \zeta_2/(1-\eta)^2$, with $\zeta_n \equiv \Sigma_{i=1}^{N} \rho_i \sigma_i^n$, $\eta \equiv (\pi/6)\zeta_3$ being the volume packing fraction.

Equations (2.21) and (2.22) give $\mathsf{L}^{(0)}$ and $\mathsf{L}^{(1)}$ as linear combinations of $\mathsf{L}^{(2)}$, $\mathsf{L}^{(3)}$, and α. We have the freedom to choose $\mathsf{L}^{(3)}$ and α, but $\mathsf{L}^{(2)}$ is constrained by the condition (2.10), i.e., the ratio second term to first term in the expansion of $\exp(\sigma_{ij} s) G_{ij}(s)$ for large s must be exactly equal to $12\tau_{ij}\sigma_{ij}$.

A. First-order approximation

The simplest approximation consists of making $\alpha = 0$. In view of the condition $e^{\sigma_{ij} s} G_{ij}(s) \sim s^0$ for large s, this implies $L_{ij}^{(3)} = 0$. In that case, the large-s behavior that follows from Eq. (2.13) is

$$2\pi e^{\sigma_{ij} s} G_{ij}(s) = L_{ij}^{(2)} + [L_{ij}^{(1)} + (\mathsf{L}^{(2)} \cdot \mathsf{D})_{ij}] s^{-1} + \mathscr{O}(s^{-2}), \tag{2.23}$$

where

$$D_{ij} \equiv \rho_i \left(\frac{1}{2} \sigma_i^2 L_{ij}^{(0)} - \sigma_i L_{ij}^{(1)} + L_{ij}^{(2)} \right). \tag{2.24}$$

Comparison with Eq. (2.10) yields

$$y_{ij}(\sigma_{ij}) = \frac{6\tau_{ij}}{\pi \sigma_{ij}^2} L_{ij}^{(2)}, \tag{2.25}$$

$$\frac{12\tau_{ij} L_{ij}^{(2)}}{\sigma_{ij}} = L_{ij}^{(1)} + \sum_{k=1}^{N} L_{ik}^{(2)} D_{kj}. \tag{2.26}$$

Taking into account Eqs. (2.21) and (2.22) (with $L_{ij}^{(2)} = L_{ji}^{(2)}$ and of course also with $\alpha = 0$ and $\mathsf{L}^{(3)} = 0$), Eq. (2.26) becomes a closed quadratic equation for $\mathsf{L}^{(2)}$,

$$\frac{12\tau_{ij} L_{ij}^{(2)}}{\sigma_{ij}} = \lambda \sigma_{ij} + \frac{1}{2} \lambda' \sigma_i \sigma_j - \frac{1}{2} \lambda \sum_{k=1}^{N} \rho_k \sigma_k (L_{ki}^{(2)} \sigma_j + L_{kj}^{(2)} \sigma_i) + \sum_{k=1}^{N} \rho_k L_{ki}^{(2)} L_{kj}^{(2)}. \tag{2.27}$$

This closes the problem. Once $L_{ij}^{(2)}$ is known, Eq. (2.25) gives the contact values.

This first-order approximation obtained from the RFA method turns out to coincide with the exact solution of the PY theory for SHS.[4]

B. Second-order approximation

A more flexible proposal is obtained by keeping α (and, consequently, $L_{ij}^{(3)}$) different from zero. In that case,

$$2\pi e^{\sigma_{ij} s} G_{ij}(s) = \frac{L_{ij}^{(3)}}{\alpha} \left[1 + \left(\frac{L_{ij}^{(2)}}{L_{ij}^{(3)}} - \frac{1}{\alpha} \right) s^{-1} \right] + \mathscr{O}(s^{-2}). \tag{2.28}$$

This implies

$$y_{ij}(\sigma_{ij}) = \frac{6\tau_{ij}}{\pi \sigma_{ij}^2} \frac{L_{ij}^{(3)}}{\alpha}, \tag{2.29}$$

$$\frac{12\tau_{ij} L_{ij}^{(3)}}{\sigma_{ij}} = L_{ij}^{(2)} - \frac{L_{ij}^{(3)}}{\alpha}. \tag{2.30}$$

If we fix $y_{ij}(\sigma_{ij})$, Eqs. (2.21), (2.22), (2.29), and (2.30) allow one to express $\mathsf{L}^{(0)}$, $\mathsf{L}^{(1)}$, $\mathsf{L}^{(2)}$, and $\mathsf{L}^{(3)}$ as *linear* functions of α. Thus, only the scalar parameter α remains to be fixed. One possibility is to choose this parameter in order to reproduce a given thermodynamic property. Following the route of our previous work,[10,11] we take the isothermal susceptibility χ. To do so, one needs first to find the coefficients $H_{ij}^{(0)}$ and $H_{ij}^{(1)}$ appearing in Eq. (2.11). Performing a power series expansion of $G_{ij}(s)$, as given by Eq. (2.13), and comparing with Eq. (2.11), one gets

$$\mathsf{H}^{(0)} = \mathsf{B}^{(0)} \cdot (\mathbb{1} - \mathsf{A}^{(0)})^{-1}, \tag{2.31}$$

$$\mathsf{H}^{(1)} = \mathsf{B}^{(1)} \cdot (\mathbb{1} - \mathsf{A}^{(0)})^{-1}, \tag{2.32}$$

where

$$B_{ij}^{(0)} = \frac{1}{2\pi} L_{ij}^{(2)} + \sum_{k=1}^{N} A_{kj}^{(2)} - \sum_{k=1}^{N} \sigma_{ik} (\alpha \delta_{kj} - A_{kj}^{(1)}) - \sum_{k=1}^{N} \frac{1}{2} \sigma_{ik}^2 (\delta_{kj} - A_{kj}^{(0)}), \tag{2.33}$$

$$B_{ij}^{(1)} = \frac{1}{2\pi} L_{ij}^{(3)} + \sum_{k=1}^{N} A_{kj}^{(3)} + \sum_{k=1}^{N} \sigma_{ik} A_{kj}^{(2)} - \sum_{k=1}^{N} \left(\frac{1}{2} \sigma_{ik}^2 + H_{ik}^{(0)} \right) (\alpha \delta_{kj} - A_{kj}^{(1)}) - \sum_{k=1}^{N} \left(\frac{1}{6} \sigma_{ik}^3 + \sigma_{ik} H_{ik}^{(0)} \right) (\delta_{kj} - A_{kj}^{(0)}). \tag{2.34}$$

Equation (2.32) gives $\mathsf{H}^{(1)}$ in terms of α; $H_{ij}^{(1)} = P_{ij}(\alpha)/[Q(\alpha)]^2$, 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 susceptibility 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 (2.7) may be rewritten as $\mathbb{1}-\hat{c}(q)=[\mathbb{1}+\hat{h}(q)]^{-1}$. Therefore,

$$\chi^{-1}=\sum_{i=1}^{N}\sum_{j=1}^{N}\sqrt{x_ix_j}[\delta_{ij}-\hat{c}_{ij}(0)]$$
$$=\sum_{i=j}^{N}\sum_{j=1}^{N}\sqrt{x_ix_j}[\mathbb{1}+\hat{\mathsf{h}}(0)]_{ij}^{-1}. \tag{2.35}$$

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 $2N$. Given a value of χ, one may solve for α using Eq. (2.35). It turns out that the physical solution, which has to fulfill the requirement that $G_{ij}(s)$ is positive definite for positive real s, corresponds to the smallest positive real root.

Once α is known, the scheme is complete; Eq. (2.29) gives $\mathsf{L}^{(3)}$, then $\mathsf{L}^{(2)}$ is obtained from Eq. (2.30), and finally $\mathsf{L}^{(1)}$ and $\mathsf{L}^{(0)}$ are given by Eqs. (2.21) and (2.22), respectively. Explicit knowledge of $G_{ij}(s)$ through Eq. (2.13) allows us to determine immediately the Fourier transform $\tilde{h}_{ij}(q)$ through the relation

$$\tilde{h}_{ij}(q)=-4\pi\sigma_{ij}^3\ \mathrm{Re}\left.\frac{s^2G_{ij}(s)-1}{s^3}\right|_{s=\mathrm{i}q}. \tag{2.36}$$

The structure factor $S_{ij}(q)$ may be expressed in terms of $\tilde{h}_{ij}(q)$ as[15]

$$S_{ij}(q)=x_i\delta_{ij}+\rho x_ix_j\tilde{h}_{ij}(q). \tag{2.37}$$

Finally, inverse Laplace transformation of $G_{ij}(s)$ yields $g_{ij}(r)$.[16]

III. ILLUSTRATIVE EXAMPLES

Up to here, the presentation is rather general. However, the practical implementation of the method requires $y_{ij}(\sigma_{ij})$ and α (or equivalently χ). In this case and in contrast with the one of the multicomponent HS mixture,[11] we have neither an approximate (analytical) equation of state nor computer simulations to guide us in their choice. Therefore, in order to proceed further, we will adopt a particular strategy in which the main aim will be to illustrate the possible use of our formulation and its likely connection with realistic systems such as colloidal systems.

We start by recalling that in the case of a one-component fluid, the comparison between the Monte Carlo data and the PY approximation indicates that the latter fails to perform well at low temperatures even at low densities. This applies both to structural as well as thermodynamic properties.[13,17] It should be expected that as the temperature increases, the performance of the PY results for the one-component SHS system should become close to the ones of the well-known HS case, which are known to deviate from simulations at high densities.[18] In the case of HS mixtures, similar limitations of the PY approximation have been found, particularly for the radial distribution functions around the contact region.[19] It is not unreasonable therefore to expect that similar drawbacks of the PY approximation will be present for SHS mixtures. Nevertheless, we conjecture that the main source of such limitations, especially for high temperatures, comes from the poor performance of the PY in the purely HS system and that a (reasonable) order of magnitude estimate of the differences between the structural and thermodynamic properties of the sticky system and those of the purely HS system may be obtained from the PY approximation. Thus, we will now consider the following approximation

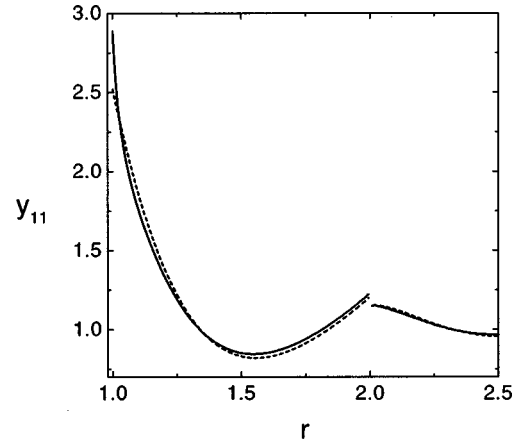

FIG. 1. Cavity correlation function $y_{11}(r)$ for the binary sticky-hard-sphere mixture defined by $\sigma_1=\sigma_2=\sigma$, $x_1=x_2=0.5$, $\eta=0.4$, $\tau_{11}=\tau_{22}=1$, and $\tau_{12}=10$. The value of α for this mixture is 0.0202. Distances are measured in units of σ. The dashed line corresponds to the PY approximation while the solid line represents the RFA result.

$$y_{ij}(\sigma_{ij})=y_{ij}^{\mathrm{BMCSL}}(\sigma_{ij})+[y_{ij}^{\mathrm{PY\text{-}SHS}}(\sigma_{ij})-y_{ij}^{\mathrm{PY\text{-}HS}}(\sigma_{ij})] \tag{3.1}$$

and

$$\chi^{-1}=\chi_{\mathrm{BMCSL}}^{-1}+(\chi_{\mathrm{PY\text{-}SHS}}^{-1}-\chi_{\mathrm{PY\text{-}HS}}^{-1}). \tag{3.2}$$

The labels PY-SHS and PY-HS refer to the PY result for SHS mixtures[4] and the PY result for HS mixtures,[20] respectively. Here $\chi_{\mathrm{BMCSL}}^{-1}$ is obtained from the Boublík–Mansoori–Carnahan–Starling–Leland (BMCSL) equation of state,[21] and $y_{ij}^{\mathrm{BMCSL}}(\sigma_{ij})$ is the contact value of the cavity functions for HS mixtures compatible with such equation of state.[22] They are given by

$$y_{ij}^{\mathrm{BMCSI}}(\sigma_{ij})=\frac{1}{2\pi}\left(\lambda+\frac{1}{2}\lambda'\frac{\sigma_i\sigma_j}{\sigma_{ij}}+\frac{1}{18}\frac{\lambda'^2}{\lambda}\frac{\sigma_i^2\sigma_j^2}{\sigma_{ij}^2}\right), \tag{3.3}$$

$$\chi_{\mathrm{BMCSL}}^{-1}=\frac{1}{\rho}\left[\frac{\rho}{(1-\eta)^2}+\pi\frac{\zeta_1\zeta_2}{(1-\eta)^3}+\frac{\pi^2}{36}\zeta_2^3\frac{9-4\eta+\eta^2}{(1-\eta)^4}\right]. \tag{3.4}$$

The underlying philosophy is that one should start from a good description of the purely HS mixture (in this case given by the BMCSL results) to get an improvement of the PY results via the procedure indicated above.

For the sake of illustration of these ideas, in Figs. 1 and 2 we present the results for the cavity functions $y_{ij}(r)$ for a

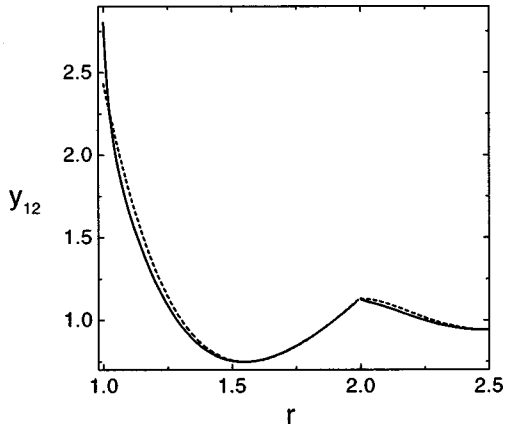

FIG. 2. The same as in Fig. 1 but for the cavity correlation function $y_{12}(r)$.

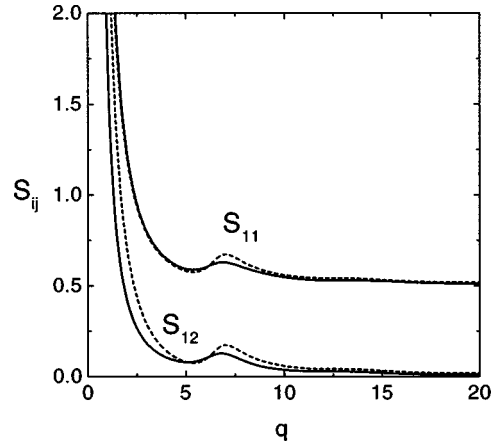

FIG. 3. Structure factors $S_{11}(q)$ and $S_{12}(q)$ for the binary sticky-hard-sphere mixture defined by $\sigma_1=\sigma_2=\sigma$, $x_1=x_2=0.5$, $\eta=0.4, \tau_{11}=\tau_{22}=0.5$, $\tau_{12}\to\infty$, and $\chi=0.05$. In this case, $\alpha=0.1343$. The wave number q is measured in units of σ^{-1}. The solid line represents the RFA result while the dashed line corresponds to the PY approximation for the effective mixture ($\tilde{\eta}=0.424$, $\tilde{\tau}_{11}=\tilde{\tau}_{22}=0.9$, $\tilde{\tau}_{12}\to\infty$).

particularly simple binary SHS mixture defined by $\sigma_1=\sigma_2=\sigma$, $x_1=x_2=0.5$, $\eta=0.4$, $\tau_{11}=\tau_{22}=1$, and $\tau_{12}=10$. For comparison, in the same figures we have included the corresponding results using the PY approximation. We find that the behavior of these functions is similar to the one we observed in the case of the the HS mixtures,[11] which is not surprising in view of the fact that the values of the τ_{ij} are relatively big, but not so as to make the discontinuities at $r=2\sigma$ disappear completely. In the absence of simulation data to compare with, it is not possible to ascertain whether the RFA results are better or worse than the PY values. One would expect however that, for this particular mixture and given its closeness to a pure HS mixture, our results should be the better ones.

We now turn to a second example. In this case we are motivated by an approach already used for colloids.[9] Consider a given real fluid mixture in which, by whatever means, we knew the total density ρ, the adhesiveness parameters of the equivalent SHS system $\{\tau_{ij}\}$ (for whose determination different strategies have been suggested in the literature[7,23]), the sizes of each species $\{\sigma_i\}$, the molar fractions $\{x_i\}$, the isothermal compressibility χ, and the coordination numbers at a prescribed distance $\lambda_{ij}\sigma_{ij}$ defined by

$$N_{ij}=4\pi\rho_i\int_{\sigma_{ij}}^{\lambda_{ij}\sigma_{ij}}dr\ r^2 g_{ij}(r). \tag{3.5}$$

Then, in order to make use of the RFA method, we determine the values of $y_{ij}(\sigma_{ij})$ and α of the SHS mixture in such a way as to reproduce the given values of N_{ij} and χ. This procedure has some parallels with the one of Amokrane and Regnaut,[9] in which the roles played by our $y_{ij}(\sigma_{ij})$ and α would be played by ''effective parameters'' $\tilde{\tau}_{ij}$ and $\tilde{\eta}$ in the PY approximation. To illustrate the kind of results that one would get through this path, we have taken again a simple binary SHS mixture defined by $\sigma_1=\sigma_2=\sigma$, $x_1=x_2=0.5$, $\eta=0.4$, $\tau_{11}=\tau_{22}=0.5$, $\tau_{12}\to\infty$, $N_{11}=N_{22}\simeq 5.67$, $N_{12}\simeq 3.9$, $\lambda_{ij}=1.5$, and $\chi=0.05$. In Fig. 3 we present the partial structure factors S_{11} and S_{12} as functions of the wave number q obtained with the above procedure. As a matter of fact, what we actually did for the sake of simplicity was to start from the values $y_{11}(\sigma)=y_{22}(\sigma)=2.0$, $y_{12}(\sigma)=1.75$ and $\chi=0.05$, and then computed the corresponding N_{ij} with $\lambda_{ij}=1.5$. We then determined the effective parameters of the Amokrane and Regnaut approximation that leads to the same coordination number N_{11} and isothermal compressibility, yielding $\tilde{\eta}=0.424$ and $\tilde{\tau}_{11}=\tilde{\tau}_{22}=0.9$. In deriving these results, we have assumed for simplicity that the effective parameter $\tilde{\tau}_{12}$ retains the character of the HS interaction between the two species. The results for this effective mixture in the PY approximation are also plotted in Fig. 3. Since once again there are no simulation data to compare with, no conclusions can be directly drawn from the numerical differences. It must be emphasized though that in the RFA method we *do not* have to determine effective parameters and so both the density and adhesiveness in our case would be the ones obtained through the standard mapping[7,23] of the real potentials.

IV. DISCUSSION

In this paper we have presented a rational function approximation method for the computation of the the radial distribution functions (in Laplace space) and structure factors of a SHS mixture. In its simplest implementation the method yields the PY approximation for an N-component SHS mixture. The next order, which we may refer to as a kind of GMSA for this system and which follows rather closely the development that we introduced earlier[11] for purely (additive) HS mixtures, provides analytic expressions in Laplace space for the radial distribution functions $g_{ij}(r)$ and the structure factors $S_{ij}(q)$ in terms of the number densities $\{\rho_i\}$, the diameters $\{\sigma_i\}$, and the adhesiveness parameters $\{\tau_{ij}\}$. As input, we require the knowledge of the contact values $y_{ij}(\sigma_{ij})$ and the isothermal susceptibility χ (although other different quantities could also be employed). Given the values of those quantities, 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 $\sigma_i=\sigma$ and $\tau_{ij}=\tau$, our approach reduces to the earlier results[12] for the SHS fluid, as it should. A similar comment can be made regarding the purely HS mixture, in that in the limit $\tau_{ij}\to\infty$ we also recover the results reported in Ref. 11.

It is worth pointing out that, as mentioned in the Introduction, we are not aware of the availability of the GMSA for a multicomponent mixture of sticky hard spheres. Nevertheless, the analytical solution to the Ornstein–Zernike equation for a multicomponent adhesive hard-core Yukawa fluid by Ginoza and Yasutomi[24] could be used for its derivation, in much the same way as Giunta, Abramo, and Caccamo[25] carried out the connection of the GMSA solution for mixtures of hard spheres with the Yukawa closure to the multicomponent HS mixture, as originally suggested by Blum and Høye.[26] We anticipate, however, that the algebraic complications involved in such a connection and that we discussed at length in Ref. 11 will also manifest themselves in this case.

It could be argued that our method presents a limitation as compared with the PY approximation in that the latter does not require any external input. However, that such is not strictly the case can be judged by the following. On the other hand, the problem of the absence of thermodynamic consistency in the PY theory may be in principle tackled with our approach, or at least reduced, as was shown for the multicomponent HS mixture.[11] On the other hand, one could expect that in some instances, as the second example of Sec. III suggests, the availability of adjustable quantities as our $y_{ij}(\sigma_{ij})$ and α may turn out to be an asset rather than a drawback.

As a final point, we would like to comment that there is still a severe scarcity of simulation data on fluid mixtures. In this sense, and due to the popularity of SHS systems to model real fluids and of the need to test approximate theories, we would hope that the present results serve as yet another motivation to perform computer simulations on SHS mixtures.

ACKNOWLEDGMENTS

S.B.Y. and A.S. acknowledge partial support from the DGES (Spain) through Grant No. PB97-1501 and from the Junta de Extremadura-Fondo Social Europeo through Grant No. PRI97C1041. The work of M.L.H. is partially supported by D.G.A.P.A.-U.N.A.M. under Project No. IN103797. S.B.Y. is grateful to the Centro de Investigación en Energía, U.N.A.M., for its hospitality during a visit in the spring of 1998. Special thanks are also due to Professor G. Stell for providing some useful references and for an enlightening discussion on the difficulties associated with the sticky-hard-sphere model.

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