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RADIAL DISTRIBUTION FUNCTIONS IN HARD-SPHERE MIXTURES *

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As is well known, hard-sphere systems play a fundamental role in the study of liquids at equilibrium, not only from a theoretical point of view, but also because they are frequently used as reference systems in perturbation theories. Therefore, it is of paramount interest to have simple and accurate expressions for the radial distribution function of those systems in the whole range of densities corresponding to the fluid phase. The problem is especially intricate in the case of an N-component mixture made of ρ_i hard spheres (of diameter σ_i) per volume unit, where $i = 1, \ldots, N$. In that case, there exist $N(N+1)/2$ radial distribution functions $g_{ij}(r)$ and $2N-1$ independent parameters characterizing the mixture (for instance, the $N-1$ molar fractions x_i, the $N-1$ size ratios σ_i/σ_1, and the packing fraction $\eta = \frac{\pi}{6}\sum_i \rho_i \sigma_i^3$). A quite good approximation is given by Lebowitz's [2] exact solution of the Ornstein-Zernike equation with the Percus-Yevick (PY) closure, namely $c_{ij}(r) = 0$ for $r > \sigma_{ij} \equiv (\sigma_i + \sigma_j)/2$, where $c_{ij}(r)$ are the direct correlation functions. Nonetheless, comparison with simulation data shows the existence of some deficiencies, similar to those already found in the one-component case. A remarkable improvement is obtained by means of the "Generalized Mean Spherical Approximation" (GMSA) [1], in which the closure relation reads $c_{ij}(r) = K_{ij} e^{-zr}/r$ for $r > \sigma_{ij}$; the parameters K_{ij} and z can be chosen by imposing, for example, given values for $g_{ij}(\sigma_{ij}^+)$ and for the isothermal compressibility κ_T. However, the practical implementation of the GMSA requires to solve, on the one hand, two *nonlinear* sets N^2 equations each (for given K_{ij} and z) and, on the other hand, a *nonlinear* set of $N(N+1)/2+1$ equations in order to get K_{ij} and z from $g_{ij}(\sigma_{ij}^+)$ and κ_T.

In this work we briefly describe an alternative method to obtain $g_{ij}(r)$ which, while giving results equivalent to those of the GMSA, is much simpler to implement. This method [4] is an extension to mixtures of the one previously applied to one-component systems of hard spheres, sticky hard spheres, and square wells [3]. As happens in the PY and GMSA theories, it is convenient to work in the Laplace space and define $G_{ij}(s) = \int_0^\infty dr\, e^{-sr} r g_{ij}(r)$. There are two basic requirements that $G_{ij}(s)$ must satisfy. First, $g_{ij}(r) = 0$ for $r < \sigma_{ij}$ and $g_{ij}(\sigma_{ij}^+) =$ finite, which implies that (i) $\lim_{s\to\infty} s e^{s\sigma_{ij}} G_{ij}(s) =$ finite. Second, $\kappa_T =$ finite, so that (ii) $\lim_{s\to 0}[G_{ij}(s) - s^{-2}] =$ finite. The approximation we propose consists of assuming the following functional form:

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

where $L_{ij}(s) = L_{ij}^{(0)} + L_{ij}^{(1)} s + L_{ij}^{(2)} s^2$ and $A_{ij}(s) = \rho_i \sum_{n=0}^2 \varphi_n(s\sigma_i)\sigma_i^{n+1} L_{ij}^{(2-n)}$, with $\varphi_n(x) \equiv x^{-(n+1)}[\sum_{m=0}^n (-x)^m/m! - e^{-x}]$. Condition (i) is verified by construction.

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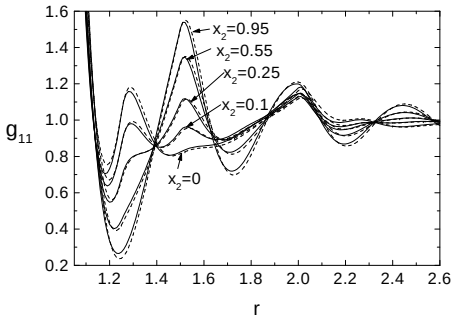

FIG. 1. Plot of $g_{11}(r)$ for ternary mixtures with $\eta = 0.49$, $\sigma_1 = 1$, $\sigma_2 = 0.5$, $\sigma_3 = 0.25$, $x_1 = 0.05$, and $x_2 = 0, 0.1, 0.25, 0.55, 0.95$. The solid and dashed lines correspond to this work and the PY solution, respectively.

On the other hand, condition (ii) yields two *linear* sets of N^2 equations each, whose solution is straightforward: $L_{ij}^{(0)} = \lambda + \lambda'\sigma_j + 2\lambda'\alpha - \lambda\sum_k \rho_k\sigma_k L_{kj}^{(2)}$, $L_{ij}^{(1)} = \lambda\sigma_{ij} + \frac{\lambda'}{2}\sigma_i\sigma_j + (\lambda+\lambda'\sigma_i)\alpha - \frac{\lambda}{2}\sigma_i\sum_k \rho_k\sigma_k L_{kj}^{(2)}$, 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 α (which play a role similar to that of the parameters K_{ij} and z in the GMSA) are arbitrary, so that conditions (i) y (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 $L_{ij}^{(2)} = 2\pi\alpha\sigma_{ij}g_{ij}(\sigma_{ij}^+)$; thus, only α remains to be determined. Finally, if we fix κ_T, we obtain a closed equation for α of degree $2N$. The comparison with simulation data shows a significant improvement of the results obtained from our method (by using the values of $g_{ij}(\sigma_{ij}^+)$ and κ_T given by the BMCSL equation of state) with respect to the PY solution, particularly in the vicinity of the contact points. In addition, we have verified that in the binary case a high degree of consistency between the five thermodynamics routes to the equation of state exists. For details, see Ref. [4]. As a complement to the cases considered in Ref. [4], we plot in Fig. 1 the radial distribution function $g_{11}(r)$ for several ternary mixtures.

The work reported here and in Ref. [4] can be extended in a number of directions. For instance, one could use as input an equation of state different from the BMCSL (e.g., one predicting the demixing transition) and analyze its influence on the structure of the mixture. It is also possible to apply the same approach to mixtures of particles interacting via the sticky-hard-sphere model or, more generally, via the square-well interaction A more difficult, but yet quite interesting, situation is that of non-additive mixtures.

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