Contact values of the radial distribution functions of additive hard-sphere mixtures in *d* dimensions: A new proposal

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The contact values $g_{ij}(\sigma_{ij})$ of the radial distribution functions of a d-dimensional mixture of (additive) hard spheres are considered. A ''universality'' assumption is put forward, according to which $g_{ij}(\sigma_{ij})=G(\eta,z_{ij})$, where G is a common function for all the mixtures of the same dimensionality, regardless of the number of components, η is the packing fraction of the mixture, and $z_{ij}=(\sigma_i\sigma_j/\sigma_{ij})\langle\sigma^{d-1}\rangle/\langle\sigma^d\rangle$ is a dimensionless parameter, $\langle\sigma^n\rangle$ being the nth moment of the diameter distribution. For $d=3$, this universality assumption holds for the contact values of the Percus–Yevick approximation, the scaled particle theory, and, consequently, the Boublík–Grundke–Henderson–Lee–Levesque approximation. Known exact consistency conditions are used to express $G(\eta,0)$, $G(\eta,1)$, and $G(\eta,2)$ in terms of the radial distribution at contact of the one-component system. Two specific proposals consistent with the above-mentioned conditions (a quadratic form and a rational form) are made for the z dependence of $G(\eta,z)$. For one-dimensional systems, the proposals for the contact values reduce to the exact result. Good agreement between the predictions of the proposals and available numerical results is found for $d=2$, 3, 4, and 5. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1502247]

I. INTRODUCTION

It is well-known that there exists a close connection between the thermodynamic and structural properties of classical fluids. In fact, for pairwise additive intermolecular potentials, all the thermodynamic functions may be expressed in terms of the radial distribution functions (rdf). The expressions are particularly simple for hard-core fluids, since in that case the internal energy reduces to that of the ideal gas and in the pressure equation it is only the contact values rather than the full rdf which appear explicitly. Therefore, knowledge of the contact values of the rdf in hard-core fluids, which we will denote by $g_{ij}(\sigma_{ij})$ (where in general i and j label species and σ_{ij} is the distance of separation at contact between the centers of two interacting fluid particles, one of species i and the other of species j), suffices to obtain the equation of state (EOS) of these systems. In the case of a single component hard-core fluid, if the EOS were known then it would be straightforward to infer the contact value of the radial distribution function. In contrast, if one were given the EOS of a multicomponent hard-core mixture such contact values could not be determined in a unique way. To this day, no exact expressions for the contact values of the rdf or for the EOS (except for the case of one-dimensional systems, i.e., hard rods) are known, although various approximate theories, empirical efforts, and computer simulations have been carried out in connection with this problem. One-component systems are, of course, easier to handle and this has meant that studies for mixtures are much more scarce. Perhaps the most successful theoretical (analytical) approach to this issue in the case of additive hard-sphere mixtures ($d=3$) is the exact solution of the Percus–Yevick (PY) equation carried out by Lebowitz in 1964.[1] This analytical solution, which among other things yields explicit expressions for the contact values of the rdf, as well as for the virial and the compressibility routes to the EOS, is at the basis of the celebrated (and empirically derived) Boublík–Mansoori–Carnahan–Starling–Leland (BMCSL) EOS,[2,3] considered to be a rather accurate EOS for hard-sphere mixtures. In his paper,[2] Boublík also introduced an approximation for the contact values of the rdf [in fact an interpolation between the PY results and the ones of the scaled particle theory (SPT)[4,5]] that later was independently proposed by Grundke and Henderson[6] and Lee and Levesque.[7] This approximation, which we will refer to as BGHLL, leads precisely to the BMCSL EOS when substituted into the statistical mechanical formula for the pressure equation. Refinements of the BGHLL approximation have recently been proposed by Henderson and Chan,[8–12] Matyushov and Ladanyi,[13] and Barrio and Solana[14] to cope with some deficiencies of the BMCSL EOS in the so-called colloidal limit of binary hard-sphere mixtures.

As far as we are aware, there are no reported approximations for $g_{ij}(\sigma_{ij})$ with $d\neq 3$, except that of Jenkins and Mancini[15] in the case of hard-disk mixtures and our own[16] for d-dimensional mixtures. The latter approximation, however, was introduced only as a means to derive a proposal for the EOS of mixtures. In fact, while this EOS presents an excellent agreement with simulations for $d=2$,[16,17]

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$d=3$,[16,18,19] $d=4$,[20] and $d=5$,[20] the expressions for $g_{ij}(\sigma_{ij})$ are less accurate.[19,20] It is the major aim of this paper to propose new (improved) approximate expressions for $g_{ij}(\sigma_{ij})$, for arbitrary mixtures and arbitrary dimensionality, that, apart from satisfying known consistency conditions, are sufficiently general and flexible to accommodate any given EOS for the single fluid. A key aspect of the present approach, also included in our previous work,[16] is that we will assume from the very beginning a kind of universal behavior of the contact values which at least holds also for the solution of the PY equation,[1] for the SPT approximation,[4,5] and for the BGHLL interpolation[2,6,7] in the case of mixtures of hard spheres ($d=3$). This means that, once the dimensionality and the packing fraction are fixed, the expression for the contact values $g_{ij}(\sigma_{ij})$ for all pairs ij is the same, irrespective of the composition and the number of components in the mixture. This expression must comply with three consistency conditions related to the point particle, equal size, and the colloidal limits, respectively. Two functional forms (a quadratic one and a rational one) which are sufficiently representative will be examined. Their merits will be assessed from a comparison with available simulation data as well as with respect to the performance of the EOS obtained from them. In the latter issue, we will show that a paradoxical result is obtained. What we find is that, contrary to what one could possibly expect, better contact values *do not* necessarily mean *more accurate* EOS and that even two *different* expressions for $g_{ij}(\sigma_{ij})$ may lead to exactly the *same* EOS.

The paper is organized as follows: In Sec. II we recall the known consistency conditions and introduce the new proposals for the contact values of the rdf. Section III deals with the comparison between our contact values and ensuing EOS and simulation results. We close the paper in Sec. IV with further discussion and some concluding remarks.

II. THE PROPOSAL

Let us consider a mixture of hard spheres in d dimensions with an arbitrary number of components. The hard core of the interaction between a sphere of species i and a sphere of species j is $\sigma_{ij}=\frac{1}{2}(\sigma_i+\sigma_j)$, where the diameter of a sphere of species i is $\sigma_{ii}=\sigma_i$. The number density of the mixture is ρ and the mole fraction of species i is $x_i=\rho_i/\rho$. From these quantities one can define the packing fraction $\eta=v_d\rho\langle\sigma^d\rangle$, where $v_d=(\pi/4)^{d/2}/\Gamma(1+d/2)$ is the volume of a d-dimensional sphere of unit diameter and $\langle\sigma^n\rangle\equiv\Sigma_i x_i\sigma_i^n$ denotes the moments of the diameter distribution.

In a hard-sphere mixture, the knowledge of the contact values $g_{ij}(\sigma_{ij})$ is important for a number of reasons. For example and as stated previously, the availability of $g_{ij}(\sigma_{ij})$ is sufficient to get the equation of state (EOS) of the mixture via the virial expression

$$Z_{\mathrm{m}}(\eta)=1+2^{d-1}\eta\sum_{i,j}x_ix_j\frac{\sigma_{ij}^d}{\langle\sigma^d\rangle}g_{ij}(\sigma_{ij}), \tag{1}$$

where $Z_{\mathrm{m}}=p/\rho k_BT$ is the compressibility factor of the mixture, p being the pressure, k_B the Boltzmann constant, and T the absolute temperature. The contact values $g_{ij}(\sigma_{ij})$ are also needed to generate the entire rdf $g_{ij}(r)$ in the generalized mean spherical approximation[21] and in the rational function approximation.[22] In a different context, they are important as well to implement the Enskog kinetic theory both for elastic and inelastic hard spheres.[15,23]

The exact form of $g_{ij}(\sigma_{ij})$ as functions of the packing fraction, the set of diameters $\{\sigma_k\}$, and the set of mole fractions $\{x_k\}$ is only known in the one-dimensional case, where one simply has $g_{ij}(\sigma_{ij})=(1-\eta)^{-1}$. Consequently, for $d\geqslant 2$ one has to resort to approximate theories or empirical expressions. From that point of view, it is useful to make use of exact limit results that can help one in the construction of approximate expressions for $g_{ij}(\sigma_{ij})$. Let us consider first the limit in which one of the species, say i, is made of point particles that do not occupy volume, i.e., $\sigma_i\to 0$. In that case, $g_{ii}(\sigma_i)$ takes the ideal gas value, except that the available volume fraction is $1-\eta$:

$$\lim_{\sigma_i\to 0}g_{ii}(\sigma_i)=\frac{1}{1-\eta}. \tag{2}$$

An even simpler situation occurs when all the species have the same size, $\{\sigma_k\}\to\sigma$, so that the system becomes equivalent to a one-component system. Therefore,

$$\lim_{\{\sigma_k\}\to\sigma}g_{ij}(\sigma_{ij})=g(\sigma), \tag{3}$$

where $g(\sigma)$ is the contact value of the radial distribution function in the one-component case. Equations (2) and (3) represent the simplest and most basic conditions that $g_{ij}(\sigma_{ij})$ must satisfy. There are a number of other less trivial consistency conditions.[5,8,11,13,14,24–27] Here we consider the condition stemming from a binary mixture in which one of the species, say $i=1$, is much larger than the other one, i.e., $\sigma_1/\sigma_2\to\infty$, but occupies a negligible volume, i.e., $x_1(\sigma_1/\sigma_2)^d\to 0$. In that case, a sphere of species 1 is seen as a wall by particles of species 2, so that[8,25,28]

$$\lim_{\substack{\sigma_1/\sigma_2\to\infty\\ x_1(\sigma_1/\sigma_2)^d\to 0}}[g_{12}(\sigma_{12})-2^{d-1}\eta g_{22}(\sigma_2)]=1. \tag{4}$$

Also in that limit,[8,25,28] $\ln g_{11}(\sigma_1)\sim\sigma_1/\sigma_2$, but we will not make use of this condition here.

Our purpose now is to propose approximate expressions for $g_{ij}(\sigma_{ij})$ of hard-core mixtures with an arbitrary number of components and arbitrary dimensionality d, that satisfy the consistency conditions (2)–(4). First, we assume that the dependence of $g_{ij}(\sigma_{ij})$ on the parameters $\{\sigma_k\}$ and $\{x_k\}$ takes place *only* through the scaled quantity $z_{ij}\equiv(\sigma_i\sigma_j/\sigma_{ij})\times\langle\sigma^{d-1}\rangle/\langle\sigma^d\rangle$. More specifically,

$$g_{ij}(\sigma_{ij})=G(\eta,z_{ij}), \tag{5}$$

where the function $G(\eta,z)$ is *universal* in the sense that it is a common function for all the pairs ij, regardless of the composition and number of components of the mixture. Of course, the function $G(\eta,z)$ is different for each dimensionality d.

The ratio $\xi\equiv\langle\sigma^{d-1}\rangle/\langle\sigma^d\rangle$ can be understood as a "typical" inverse diameter or curvature of the particles of the mixture. The parameter $z_{ij}^{-1}=(\sigma_i^{-1}+\sigma_j^{-1})/2\xi$ represents then the average curvature, in units of ξ, of a particle of

species i and a particle of species j. According to Eq. (5), if two different pairs ij in two different mixtures (with the same packing fraction) have the same dimensionless average curvature z_{ij}^{-1}, then they have the same contact value of the rdf.

The ansatz (5) includes the one used by us,[16] where $G(\eta,z)$ was approximated by a linear function of z. A particular case of this linear form is the proposal made by Jenkins and Mancini for hard-disk mixtures:[15]

$$G(\eta,z)=\frac{1}{1-\eta}+\frac{9}{16}\frac{\eta}{(1-\eta)^2}z \quad (d=2). \tag{6}$$

In the three-dimensional case, Eq. (5) is also compatible with the solution of the PY equation,[1] the SPT approximation,[4,5] and, consequently, the BGHLL proposal.[2,6,7] More specifically, $G(\eta,z)$ is a linear function of z in the PY approximation and a quadratic function in the SPT and BGHLL approximations:

$$G(\eta,z)=\frac{1}{1-\eta}+\frac{3}{2}\frac{\eta}{(1-\eta)^2}z+\lambda\frac{\eta^2}{(1-\eta)^3}z^2 \quad (d=3), \tag{7}$$

where $\lambda_{\mathrm{PY}}=0$, $\lambda_{\mathrm{SPT}}=\frac{3}{4}$, and $\lambda_{\mathrm{BGHLL}}=\frac{1}{2}$. These three approximations are consistent with Eqs. (2) and (3), but only the SPT is also consistent with condition (4). The approximation referred to as the SPT-virial route by Rosenfeld[5] adopts also the scaling form (5), namely $G(\eta,z)=(1-\eta)^{-1}\exp[3z\eta/2(1-\eta)]$, but it does not comply with condition (4).

Once we adopt the ansatz (5), the limits in Eqs. (2)–(4) provide very useful constraints on the z dependence of G. First, $z_{ii}\to 0$ in the limit $\sigma_i\to 0$, so that insertion of Eq. (2) into Eq. (5) yields

$$G(\eta,0)=\frac{1}{1-\eta}. \tag{8}$$

Next, if all the diameters are equal, $z_{ij}\to 1$, so that Eq. (3) implies that

$$G(\eta,1)=g(\sigma). \tag{9}$$

Finally, in the limit considered in Eq. (4), we have $z_{22}\to 1$, $z_{12}\to 2$. Consequently,

$$G(\eta,2)=1+2^{d-1}\eta G(\eta,1). \tag{10}$$

Thus Eqs. (8)–(10) provide complete information on the function G at $z=0$, $z=1$, and $z=2$, in terms of the contact value $g(\sigma)$ of the one-component rdf.

The proposal made in Ref. 16 consists of assuming a linear dependence of G on z that satisfies the requirements (8) and (9):

$$G(\eta,z)=\frac{1}{1-\eta}+\left[g(\sigma)-\frac{1}{1-\eta}\right]z. \tag{11}$$

If in the two-dimensional case we take Henderson's value[29] $g(\sigma)=(1-7\eta/16)/(1-\eta)^2$, Eq. (11) reduces to Jenkins and Mancini's approximation,[15] Eq. (6). In general, Eq. (11) does not satisfy Eq. (10). However, the ansatz (11) was used in Ref. 16 only as a means to obtain the EOS from Eq. (1). The resulting EOS exhibits an excellent agreement with simulations in two, three, four, and five dimensions, provided that an accurate $g(\sigma)$ is used as input.[16–18,20,30] On the other hand, if one is directly interested in obtaining reliable contact values $g_{ij}(\sigma_{ij})$, then Eq. (11) is too crude. The simplest functional form of G that complies with Eqs. (8)–(10) is a quadratic function of z:

$$G(\eta,z)=G_0(\eta)+G_1(\eta)z+G_2(\eta)z^2, \tag{12}$$

where the coefficients are explicitly given by

$$G_0(\eta)=\frac{1}{1-\eta}, \tag{13a}$$

$$G_1(\eta)=(2-2^{d-2}\eta)g(\sigma)-\frac{2-\eta/2}{1-\eta}, \tag{13b}$$

$$G_2(\eta)=\frac{1-\eta/2}{1-\eta}-(1-2^{d-2}\eta)g(\sigma). \tag{13c}$$

In the one-dimensional case, Eqs. (13b) and (13c) lead to $G_1=G_2=0$ and we recover the exact result. For three-dimensional systems, if the SPT value is used for the one-component contact value, $g_{\mathrm{SPT}}(\sigma)=(1-\eta/2+\eta^2/4)/(1-\eta)^3$, we reobtain the SPT expressions for the mixture, cf. Eq. (7). On the other hand, if the much more accurate Carnahan–Starling[31] (CS) expression $g_{\mathrm{CS}}(\sigma)=(1-\eta/2)/(1-\eta)^3$ is used as input, we arrive at the following expression:

$$G(\eta,z)=\frac{1}{1-\eta}+\frac{3}{2}\frac{\eta(1-\eta/3)}{(1-\eta)^2}z+\frac{\eta^2(1-\eta/2)}{(1-\eta)^3}z^2 \quad (d=3), \tag{14}$$

which is different from the BGHLL one and improves the latter for $z>1$, as comparison with computer simulations will show. It should be noted that if one considers a binary mixture in the infinite solute dilution limit, namely $x_1\to 0$, so that $z_{12}\to 2/(1+\sigma_2/\sigma_1)$, Eq. (14) yields the same result for $g_{12}(\sigma_{12})$ as the one proposed by Matyushov and Ladanyi[13] for this quantity on the basis of exact geometrical relations. However, the extension that the same authors propose when there is a nonvanishing solute concentration, i.e., for $x_1\neq 0$ [cf. Eq. (19) in Ref. 13], is different from Eq. (14). We will come back to this point later when we assess the merits of both proposals.

Of course, the quadratic form (12) is not the only choice compatible with conditions (8)–(10). Another simple possibility is to assume a rational function of the form

$$G(\eta,z)=\frac{1+[A_1(\eta)-1]z}{B_0(\eta)+B_1(\eta)z}. \tag{15}$$

Imposing Eqs. (8)–(10), we get

$$B_0(\eta)=1-\eta, \tag{16a}$$

$$A_1(\eta)=-\frac{g(\sigma)\eta}{2}\frac{1-2^{d-1}(1-\eta)g(\sigma)}{1-(1-2^{d-1}\eta)g(\sigma)}, \tag{16b}$$

$$B_1(\eta)=-\frac{1}{2}\frac{2-\eta-(1-\eta)(2-2^{d-1}\eta)g(\sigma)}{1-(1-2^{d-1}\eta)g(\sigma)}. \tag{16c}$$

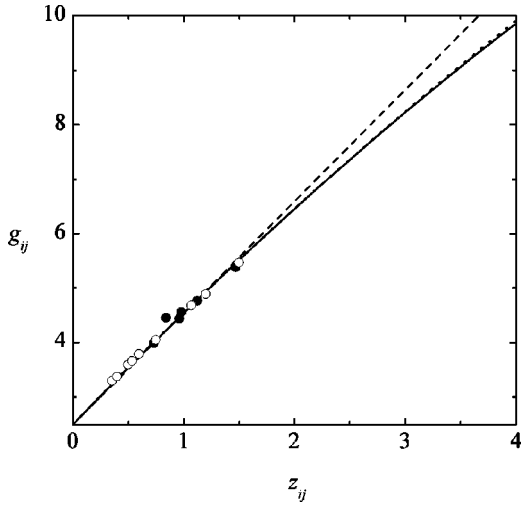

FIG. 1. Plot of the contact value $g_{ij}(\sigma_{ij})$ as a function of the parameter $z_{ij}=(\sigma_i\sigma_j/\sigma_{ij})\langle\sigma\rangle/\langle\sigma^2\rangle$ for hard disks ($d=2$) at a packing fraction $\eta=0.6$. The open circles are simulation data for three binary mixtures (Ref. 33) with $\sigma_2/\sigma_1=\frac{1}{3}$ and $x_1=0.25$, 0.5, and 0.75. The closed circles are simulation data for two binary mixtures (Ref. 34) with $\sigma_2/\sigma_1=\frac{3}{4}$ and $x_1=0.483$ and with $\sigma_2/\sigma_1=\frac{1}{2}$ and $x_1=0.219$. The lines correspond to Eq. (11) (dashed line), Eq. (12) (solid line), and Eq. (15) (dotted line).

Other functional forms for $G(\eta,z)$ complying with Eqs. (8)–(10) are possible, but the choices (12) and (15) are sufficiently representative, so we will restrict ourselves to them in this paper.

III. COMPARISON WITH SIMULATION DATA

A. Contact values of the radial distribution functions

In order to assess the utility of the new proposals for the contact values of the rdf, in Figs. 1–9 we present results for hard-core mixtures in $d=2$, 3, 4, and 5, and the available computer simulation data. Figure 1 shows $g_{ij}(\sigma_{ij})$ as a function of z_{ij} for $d=2$ and $\eta=0.6$, according to the linear approximation (11), the quadratic approximation (12), and the rational approximation (15). In the three cases we have used for $g(\sigma)$ the value obtained from the Levin [6] approximant of Erpenbeck and Luban.[32] The only tabulated simulation data for $g_{ij}(\sigma_{ij})$ in the case of hard disks that we are aware of are those of Ref. 33. Hence, we have included in Fig. 1 the simulation results for the most asymmetric mixtures considered in Ref. 33, namely $\sigma_2/\sigma_1=\frac{1}{3}$ with $x_1=0.25$, 0.5, and 0.75, and also simulation data extracted from Fig. 2 of Ref. 34. We observe that the quadratic and rational approximations, both consistent with condition (10), are hardly distinguishable. The three theoretical curves practically coincide in

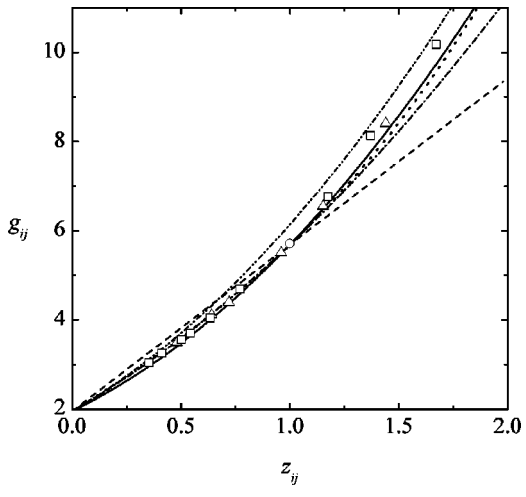

FIG. 2. Plot of the contact value $g_{ij}(\sigma_{ij})$ as a function of the parameter $z_{ij}=(\sigma_i\sigma_j/\sigma_{ij})\langle\sigma^2\rangle/\langle\sigma^3\rangle$ for hard spheres ($d=3$) at a packing fraction $\eta=0.49$. The symbols are simulation data for the single fluid (circle)—Ref. 18—three binary mixtures (squares)—Ref. 35—with $\sigma_2/\sigma_1=0.3$ and $x_1=0.0625$, 0.125, and 0.25, and a ternary mixture (triangles)—Ref. 36—with $\sigma_2/\sigma_1=\frac{2}{3}$, $\sigma_3/\sigma_1=\frac{1}{3}$ and $x_1=0.1$, $x_2=0.2$. The lines are, from bottom to top at the right end, Eq. (11) (---), BGHLL (– · –), Eq. (15) (···), Eq. (12) (——), and SPT (– ·· –).

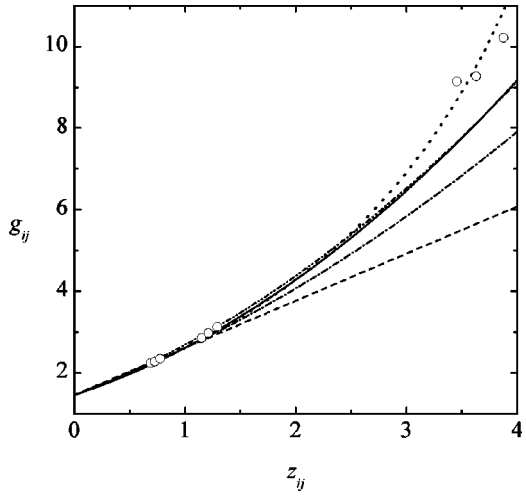

FIG. 3. Plot of the contact value $g_{ij}(\sigma_{ij})$ as a function of the parameter $z_{ij}=(\sigma_i\sigma_j/\sigma_{ij})\langle\sigma^2\rangle/\langle\sigma^3\rangle$ for hard spheres ($d=3$) at a packing fraction $\eta=0.314$. The symbols are simulation data for three binary mixtures (Ref. 19) with $\sigma_2/\sigma_1=\frac{1}{5}$ and $x_1=0.003\,11$, $0.004\,15$, and 0.005. The lines are, from bottom to top at the right end, Eq. (11) (---), BGHLL (– · –), Eq. (12) (——), SPT (– ·· –), and Eq. (15) (···).

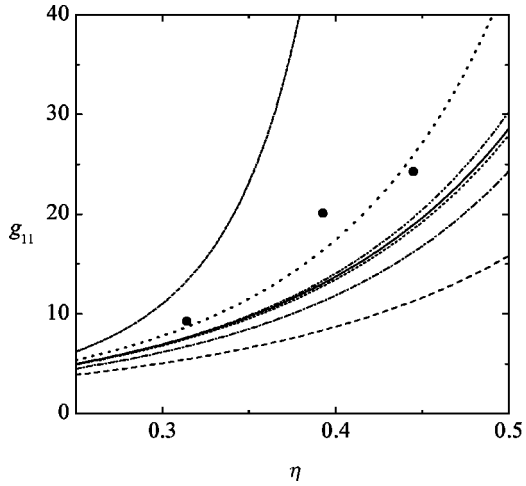

FIG. 4. Plot of the contact value $g_{11}(\sigma_1)$ as a function of the packing fraction η for the three-dimensional binary mixture $x_1=0.005$, $\sigma_2/\sigma_1=\frac{1}{5}$ ($z_{11}=3.457$). The symbols are simulation data (Ref. 19). The lines are, from bottom to top at the right end, Eq. (11) (---), BGHLL (– · –), Barrio–Solana—Ref. 14 (···), Eq. (12) (——), SPT (– ·· –), Eq. (15) (···), and Henderson–Chan—Refs. 8–11 (---).

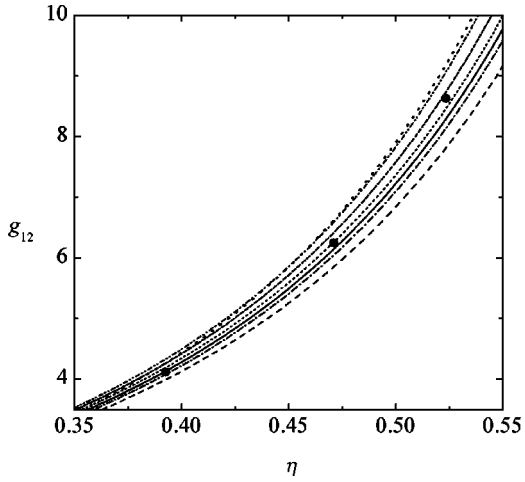

FIG. 5. Plot of the contact value $g_{12}(\sigma_{12})$ as a function of the packing fraction η for the three-dimensional binary mixture $x_1=0.004\,15$, $\sigma_2/\sigma_1=\frac{1}{5}$ ($z_{12}=1.210$). The symbols are simulation data (Ref. 19). The lines are, from bottom to top at the right end, Eq. (11) (---), BGHLL ($-\cdot-$), Eq. (12) (——), Barrio–Solana—Ref. 14 ($\cdots$), Henderson–Chan—Refs. 8–11 (---), SPT ($-\cdot\cdot-$), and Matyushov–Ladanyi—Ref. 13 ($\cdots$).

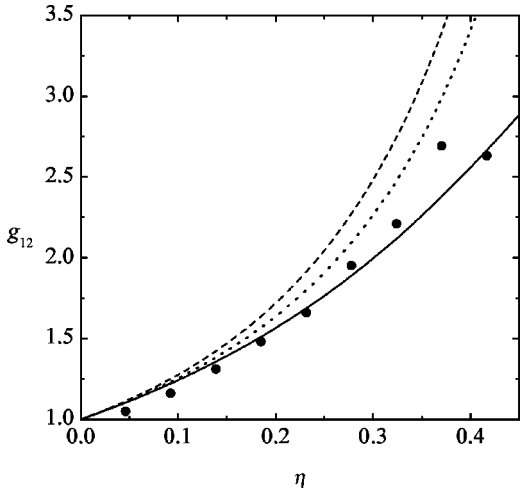

FIG. 7. Plot of the contact value $g_{12}(\sigma_{12})$ as a function of the packing fraction η for the four-dimensional binary mixture $x_1=\frac{3}{4}$, $\sigma_2/\sigma_1=0.25$ ($z_{12}=0.402$). The symbols are simulation data (Ref. 20). The lines correspond to Eq. (11) (dashed line), Eq. (15) (dotted line), and Eq. (12) (solid line).

the range of values of z_{ij} spanned by the simulations. It would be interesting to carry out simulations extending to the region $z_{ij}>2$ to assess the reliability of Eqs. (12) and (15).

A comparison between theoretical predictions and simulation values for three-dimensional mixtures is shown in Figs. 2–5. To carry out the computations in Eqs. (11), (12), and (15), we have used the CS contact value $g_{\mathrm{CS}}(\sigma)$. Figures 2 and 3 show that the universality assumption (5) is well supported by simulation data. Since the dependence of $g_{ij}(\sigma_{ij})$ on z_{ij} is nonlinear (note that the curvature is different from that of the two-dimensional case), Eq. (11) only captures some kind of ''average'' behavior. Among the three quadratic functions, namely the SPT, the BGHLL, and Eq. (12), the best global agreement is presented by Eq. (12). The SPT prescription, Eq. (7) with $\lambda=\frac{3}{4}$, is consistent with condition (10), but its performance is not very good because it is pinned at a too high value at $z=1$ (one-component case). The BGHLL prescription, Eq. (7) with $\lambda=\frac{1}{2}$, is excellent at $z=1$ (CS value), does a very good job for $0<z<1$, but clearly underestimates the simulation data for $z>1$, as expected from the fact that the BGHLL is inconsistent with Eq. (10) at $z=2$. Our recipe (12) is only slightly worse than the BGHLL for $z<1$ but improves it significantly for $z>1$. Finally, the rational function (15) is practically indistinguishable from the BGHLL for $z<1$, is reasonably good for $1<z<2$, and is the best one in the case of the large–large rdf for disparate mixtures, as shown by Fig. 3 in the region $z\approx 4$. Of course, none of these approximations is expected to be good enough in the limit of *extremely* large values of z, where $\ln G\sim z$.[8,25,28] The latter behavior could be incorpo-

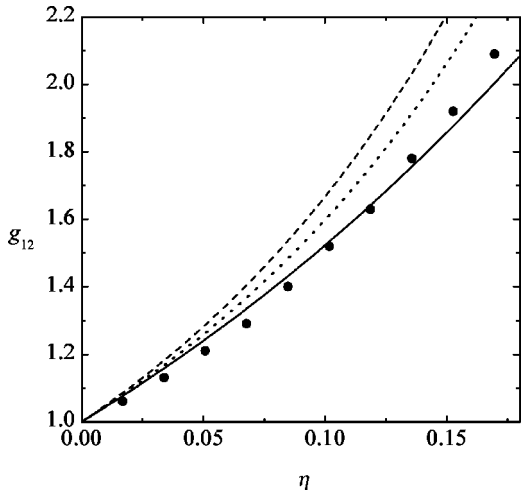

FIG. 6. Plot of the contact value $g_{12}(\sigma_{12})$ as a function of the packing fraction η for the four-dimensional binary mixture $x_1=0.5$, $\sigma_2/\sigma_1=\frac{1}{2}$ ($z_{12}=0.706$). The symbols are simulation data (Ref. 20). The lines correspond to Eq. (11) (dashed line), Eq. (15) (dotted line), and Eq. (12) (solid line).

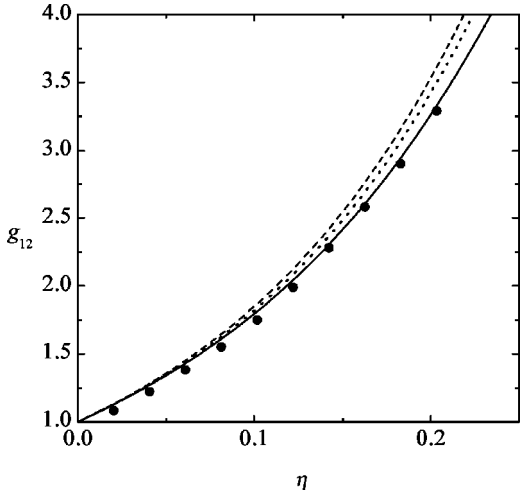

FIG. 8. Plot of the contact value $g_{12}(\sigma_{12})$ as a function of the packing fraction η for the five-dimensional binary mixture $x_1=\frac{1}{2}$, $\sigma_2/\sigma_1=0.75$ ($z_{12}=0.912$). The symbols are simulation data (Ref. 20). The lines correspond to Eq. (11) (dashed line), Eq. (15) (dotted line), and Eq. (12) (solid line).

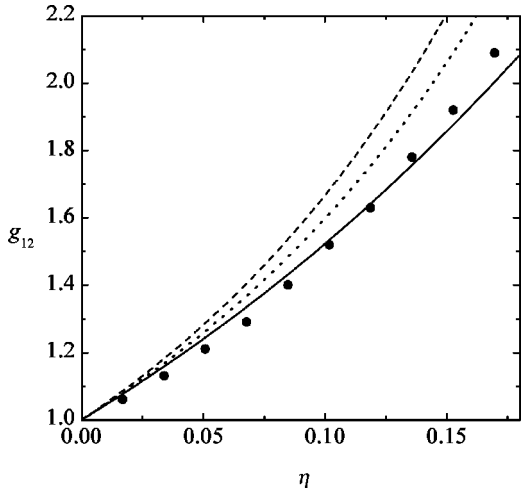

FIG. 9. Plot of the contact value $g_{12}(\sigma_{12})$ as a function of the packing fraction η for the five-dimensional binary mixture $x_1=\frac{1}{2}$, $\sigma_2/\sigma_1=0.5$ ($z_{12}=0.687$). The symbols are simulation data (Ref. 20). The lines correspond to Eq. (11) (dashed line), Eq. (15) (dotted line), and Eq. (12) (solid line).

rated by choosing an adequate functional form for $G(\eta,z)$ consistent with conditions (8)–(10), but this does not seem to be necessary in the range $0\leqslant z\leqslant 4$. Since the best global agreement in the range $0\leqslant z\leqslant 2$ is provided by the polynomial function (12), which has a structure similar to the well-known BGHLL prescription in the case of $d=3$ [cf. Eq. (14)], we favor its use, except perhaps for very disparate mixtures, where the rational approximation (15) is preferable.

The refinements of the BGHLL expressions recently proposed by Henderson and Chan[8–11] and by Barrio and Solana[14] are not shown in Figs. 2 and 3 because they do not belong to the class of approximations satisfying the universality assumption (5). In addition, they are restricted to the case of *binary* mixtures. Both approximations differ in practice from the BGHLL only in $g_{11}(\sigma_1)$, where species 1 refer to the big spheres ($\sigma_1>\sigma_2$). Figure 4 shows $g_{11}(\sigma_1)$ vs η for the three-dimensional binary mixture $x_1=0.005$, $\sigma_2/\sigma_1=\frac{1}{5}$ (which corresponds to $z_{11}=3.457$). The figure confirms that the best agreement is obtained with the rational approximation (15). Henderson and Chan's approximation, which incorporates the exact asymptotic behavior $\ln g_{11}(\sigma_1)\sim\sigma_1$, gives too high values. Barrio and Solana's expression improves the BGHLL value, but is slightly worse than the quadratic approximation (12).

Figure 5 presents a plot of $g_{12}(\sigma_{12})$ as a function of η for the three-dimensional binary mixture characterized by $x_1=0.004\,15$ and $\sigma_2/\sigma_1=\frac{1}{5}$ (which corresponds to a value of $z_{12}=1.210$) as given by different approximations. The rational approximation given by Eq. (15) has not been included in Fig. 5 to avoid overcrowding of the curves, but it is practically indistinguishable from the BGHLL approximation in this case. Clearly the best agreement between theory and simulation is provided by the approximations of Barrio and Solana,[14] of Henderson and Chan,[11] and by our Eq. (12), which are all of comparable accuracy and certainly superior to the approximation proposed in Eq. (19) of the paper by Matyushov and Ladanyi.[13]

Of course, the most physically relevant situations correspond to hard spheres ($d=3$) and, to a lesser extent, disks ($d=2$). On the other hand, it seems desirable that a proposal for $g_{ij}(\sigma_{ij})$ be valid for any dimensionality d. Moreover, a number of recent papers deal with systems of hard hyperspheres.[20,37–43] Figures 6–9 show $g_{12}(\sigma_{12})$ versus η for binary mixtures in $d=4$ and $d=5$. The contact values of the one-component system that we have used in the computations have been obtained from the EOS derived for these systems by Luban and Michels.[44] The values of the parameter z_{12} are in the range $0.4<z_{12}<1$ for the cases considered in Figs. 6–9. It is observed that in this range the quadratic approximation (12) exhibits an excellent agreement with the simulation data.

B. Equation of state

Having examined the accuracy of the proposed contact values, we will now consider their performance in terms of the compressibility factor they lead to. In this regard, Eq. (12) has the advantage over Eq. (15) that, when inserted into Eq. (1), one gets a closed expression for the compressibility factor, in terms of the packing fraction η and the first few moments $\langle\sigma^n\rangle$, $n\leqslant d$. This expression is meaningful even for polydisperse mixtures. The result is

$$Z_{\rm m}(\eta)=1+2^{d-2}\frac{\eta}{1-\eta}[2(S_0-2S_1+S_2)+(S_1-S_2)\eta]+[Z_{\rm s}(\eta)-1][2S_1-S_2+2^{d-2}(S_2-S_1)\eta], \tag{17}$$

where $Z_{\rm s}(\eta)=1+2^{d-1}\eta g(\sigma)$ is the compressibility factor of the one-component system and the coefficients S_m are given by

$$S_m=2^{-(d-m)}\frac{\langle\sigma^{d-1}\rangle^m}{\langle\sigma^d\rangle^{m+1}}\sum_{n=0}^{d-m}\binom{d-m}{n}\langle\sigma^{n+m}\rangle\langle\sigma^{d-n}\rangle. \tag{18}$$

In the two-dimensional case, Eq. (17) becomes

$$Z_{\rm m}(\eta)=\frac{1}{1-\eta}+\frac{\langle\sigma\rangle^2}{\langle\sigma^2\rangle}\left[Z_{\rm s}(\eta)-\frac{1}{1-\eta}\right]\quad(d=2). \tag{19}$$

It is worth noticing that this EOS coincides with the one obtained from Eq. (11) for $d=2$. This illustrates the fact that two different proposals for the contact values $g_{ij}(\sigma_{ij})$ can yield the same EOS when inserted into Eq. (1). Let us analyze this point with more detail. Subtracting Eqs. (11) and (12), one has

$$\Delta G(\eta,z)=\left[\frac{1-\eta/2}{1-\eta}-(1-2^{d-2}\eta)g(\sigma)\right]z(1-z), \tag{20}$$

where $\Delta G(\eta,z)$ denotes the difference between the linear and the quadratic approximations. Thus, the compressibility factors obtained from the linear and quadratic forms for $G(\eta,z)$ only differ by a term proportional to $\Sigma_{i,j}x_ix_j\sigma_{ij}^d z_{ij}(1-z_{ij})$. It turns out that this term vanishes in the two-dimensional case, so the linear and quadratic ap-

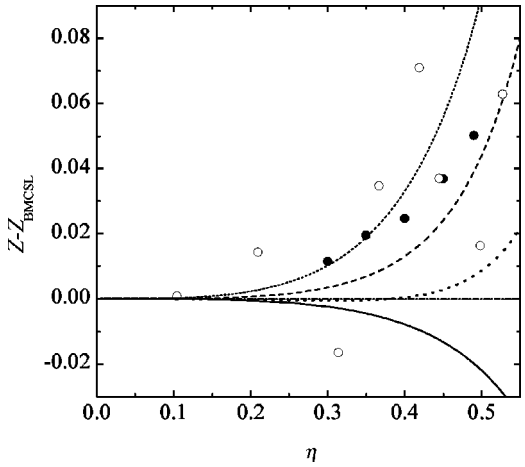

FIG. 10. Deviation of the compressibility factor from the BMCSL value, as a function of the packing fraction η for an equimolar three-dimensional binary mixture with $\sigma_2/\sigma_1=0.6$. The open (Ref. 9) and closed (Ref. 45) circles are simulation data. The lines are, from bottom to top at the right end, the eCS-II EOS (22) (——), the EOS obtained from the rational approximation (15) (···), the eCS-I EOS (24) (---), and Barrio and Solana's EOS (···)—Ref. 14.

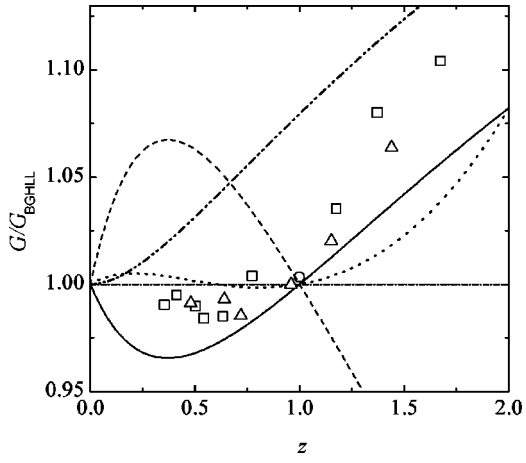

FIG. 11. Plot of the ratio $G(\eta,z)/G_{\mathrm{BGHLL}}(\eta,z)$ as a function of the parameter z for hard spheres ($d=3$) at a packing fraction $\eta=0.49$. The symbols are simulation data for the single fluid (circle)—Ref. 18—three binary mixtures (squares)—Ref. 35—with $\sigma_2/\sigma_1=0.3$ and $x_1=0.0625$, 0.125, and 0.25, and a ternary mixture (triangles)—Ref. 36—with $\sigma_2/\sigma_1=\frac{2}{3}$, $\sigma_3/\sigma_1=\frac{1}{3}$, and $x_1=0.1$, $x_2=0.2$. The lines correspond to Eq. (11) (---), Eq. (12) (——), Eq. (15) (···), and SPT (– · · –).

proximations yield the same EOS (19). This fact also shows that a rather crude approximation such as Eq. (11) may lead to an extremely good EOS.[16,17,20,30]

For three-dimensional mixtures, Eq. (17) becomes

$$Z_{\mathrm{m}}(\eta)=\frac{1}{1-\eta}+\frac{\langle\sigma\rangle\langle\sigma^2\rangle}{\langle\sigma^3\rangle}\left(1-\eta+\frac{\langle\sigma^2\rangle^2}{\langle\sigma\rangle\langle\sigma^3\rangle}\eta\right)\times\left[Z_{\mathrm{s}}(\eta)-\frac{1}{1-\eta}\right]\quad(d=3).\tag{21}$$

In particular, when the CS EOS $Z_s(\eta)=(1+\eta+\eta^2-\eta^3)/(1-\eta)^3$ is used as input, we get the following extended CS EOS:

$$Z_{\mathrm{eCS\text{-}II}}(\eta)=Z_{\mathrm{BMCSL}}(\eta)-\frac{\eta^3\langle\sigma^2\rangle}{(1-\eta)^2\langle\sigma^3\rangle^2}(\langle\sigma\rangle\langle\sigma^3\rangle-\langle\sigma^2\rangle^2),\tag{22}$$

where the compressibility factor associated with the BMCSL EOS[2,3] is given in the present notation by

$$Z_{\mathrm{BMCSL}}(\eta)=\frac{1}{1-\eta}+\frac{3\eta\langle\sigma\rangle\langle\sigma^2\rangle}{(1-\eta)^2\langle\sigma^3\rangle}+\frac{\eta^2(3-\eta)\langle\sigma^2\rangle^3}{(1-\eta)^3\langle\sigma^3\rangle^2}.\tag{23}$$

Note that Eq. (22) is different from the extended CS EOS obtained from Eq. (11), namely[16]

$$Z_{\mathrm{eCS\text{-}I}}(\eta)=Z_{\mathrm{BMCSL}}(\eta)+\frac{\eta^3\langle\sigma^2\rangle}{(1-\eta)^3\langle\sigma^3\rangle^2}(\langle\sigma\rangle\langle\sigma^3\rangle-\langle\sigma^2\rangle^2).\tag{24}$$

Since simulation data indicate that the BMCSL EOS tends to underestimate the compressibility factor, it is obvious that the performance of $Z_{\mathrm{eCS\text{-}I}}$ is, paradoxically, better than that of $Z_{\mathrm{eCS\text{-}II}}$. This is explicitly shown in Fig. 10 where, for comparison, we have also included the theoretical results that follow from the recent (very accurate) proposal by Barrio and Solana[14] for the EOS. So once again we find that better contact values do not necessarily lead to better compressibility factors, as already seen in the two-dimensional case. One plausible explanation for the better performance of $Z_{\mathrm{eCS\text{-}I}}$ with respect to $Z_{\mathrm{eCS\text{-}II}}$ might reside in the use of the CS EOS $Z_s(\eta)$, but we have checked that if the Padé [4,3] of Sanchez[46] or the very accurate EOS of Malijevský and Veverka[18] are used instead, the results do not change. Thus the source of this effect is a fortunate compensation of errors in the linear approximation (11) related to the fact that the compressibility factor involves a weighted average of the individual contact values $g_{ij}(\sigma_{ij})$ [cf. Eq. (1)]. This argument is suggested by the following observation. In Fig. 11 we present a plot of the ratio $G(\eta,z)/G_{\mathrm{BGHLL}}(\eta,z)$ as a function of z for $\eta=0.49$ with $G(\eta,z)$ given by Eqs. (11) and (12). For completeness, also the ratios corresponding to the SPT (7) and the rational approximation (15) are plotted. Properly reduced simulation results have also been included. From this plot it is fair to conclude that the approximation given by Eq. (12) is globally more accurate than those obtained with either Eq. (11) or with $G_{\mathrm{BGHLL}}(\eta,z)$ and that the BGHLL contact values are better than the linear approximation. However, the quadratic approximation *always* underestimates the simulation results (and therefore it is only natural that it will always produce an underestimation of the compressibility factor), while both the linear approximation and the BGHLL approximation overestimate the simulation results if $z_{ij}\leqslant 1$ but underestimate them if $z_{ij}\geqslant 1$. The net result is that $Z_{\mathrm{eCS\text{-}II}}(\eta)$ is in poorer agreement with the simulation results for the compressibility factor than either $Z_{\mathrm{eCS\text{-}I}}(\eta)$ or $Z_{\mathrm{BMCSL}}(\eta)$, the extended CS EOS obtained from Eq. (11) providing the best overall agreement. Nevertheless, an important asset of $Z_{\mathrm{eCS\text{-}II}}$, not shared by either $Z_{\mathrm{eCS\text{-}I}}$ or Z_{BMCSL}, is that it predicts demixing. This result provides further support to the analysis performed by Regnaut, Dyan, and Amokrane[28] in which the verification of

condition (4) is of key importance for the existence of demixing. We will address this issue in more detail elsewhere.

For $d=4$ and $d=5$ (not shown), however, the compressibility factors derived from the linear approximation given by Eq. (11)[16] turn out to be slightly less accurate than those obtained from the use of either Eq. (12) or Eq. (15). Thus, for these high dimensionalities, the expectation that a better overall behavior of the contact values correlates with a better performance of the associated EOS actually holds true.

IV. CONCLUSION

In summary, in this paper we have introduced a universality assumption, Eq. (5), for the contact values of the rdf of a hard-sphere mixture with arbitrary number of components and arbitrary dimensionality. Three known consistency conditions, Eqs. (2)–(4), allow us to fix the values of the universal function $G(\eta,z)$ at $z=0$ [cf. Eq. (8)], $z=1$ [cf. Eq. (9)], and $z=2$ [cf. Eq. (10)], the two latter in terms of the contact value of the one-component rdf. This implies that any reasonable three-parameter form of $G(\eta,z)$ as a function of z can provide a very good approximate representation of $g_{ij}(\sigma_{ij})$ regardless of the number of components, provided a good EOS for the single fluid system is used. We have illustrated this possibility with two specific proposals: a quadratic function, Eq. (12), and a rational function, Eq. (15). In $d=1$, they reduce to the exact result, while for $d=3$ they represent an improvement over the BGHLL values, as well as over those of their refinements, in the quantitative agreement with the simulation results. For $d=2$, 4, and 5, they compare rather well with the (few) available simulation results. Their potential use in connection with the generation of the entire rdf $g_{ij}(r)$ for three-dimensional mixtures within the rational function approximation method is currently under investigation.

The relationship between the thermodynamic properties and the contact values of the rdf in hard-core fluids is in principle so straightforward that the importance of explicit and accurate approximations for the latter can be hardly overemphasized. In one-component hard-core systems it is certainly true that a more accurate contact value of the rdf leads directly to a better EOS. On the other hand, our results in this paper indicate that, due to the fact that for mixtures the EOS (or equivalently the compressibility factor) involves a summation over species indices in which the different contact values are included, one does not *always* obtain a more accurate EOS from seemingly better approximations to $g_{ij}(\sigma_{ij})$. In fact, as exemplified in the case of hard-disk mixtures $(d=2)$, it is possible to obtain exactly the same EOS with two different approximations for the contact values of the rdf. Further, the poorer agreement of $Z_{\mathrm{eCS\text{-}II}}$ with simulation data than either $Z_{\mathrm{eCS\text{-}I}}$ or Z_{BMCSL} mentioned in Sec. III is also a reflection of the above-given assertion, the reason resting on a ''fortunate'' compensation of errors. In any event, in some specific applications (e.g., the Enskog kinetic theory) it is only the contact values of the rdf that are required. In this respect, it is fair to conclude that our two new proposals provide in general a reasonably accurate approximation to $g_{ij}(\sigma_{ij})$ (as compared to the available simulation data) for a hard-core mixture with an arbitrary number of components and arbitrary dimensionality. Of course the scarcity of simulation results for these systems precludes a more definite conclusion. In any case, we hope that the availability of the new (explicit) expressions for the contact values of the rdf of hard-core mixtures in any dimensionality may serve as a further motivation to carry out yet more simulations of these systems.

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