Equation of state of nonadditive *d*-dimensional hard-sphere mixtures

A. Santos,[a] M. López de Haro,[b] and S. B. Yuste[c]
Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain

(Received 17 September 2004; accepted 21 October 2004; published online 23 December 2004)

An equation of state for a multicomponent mixture of nonadditive hard spheres in d dimensions is proposed. It yields a rather simple density dependence and constitutes a natural extension of the equation of state for *additive* hard spheres proposed by us [A. Santos, S. B. Yuste, and M. López de Haro, Mol. Phys. **96**, 1 (1999)]. The proposal relies on the known exact second and third virial coefficients and requires as input the compressibility factor of the one-component system. A comparison is carried out both with another recent theoretical proposal based on a similar philosophy and with the available exact results and simulation data in $d=1$, 2, and 3. Good general agreement with the reported values of the virial coefficients and of the compressibility factor of binary mixtures is observed, especially for high asymmetries and/or positive nonadditivities.
 [DOI: 10.1063/1.1832591]

I. INTRODUCTION AND A BRIEF REVIEW OF THE LITERATURE

The structure of a dense fluid is known to be largely determined by the repulsive intermolecular forces, so it is not surprising that hard-core potentials have been extensively employed to model simple fluids and fluid mixtures. A noteworthy aspect of these models is the fact that in some instances both exact and approximate analytical results may be derived for the structural and thermodynamic properties, which in turn serve as a starting point for the treatment of more sophisticated or complex models.

Certainly a vast majority of the published work on hard-core (rods, disks, spheres, and hyperspheres) fluid mixtures pertains to binary systems and to the so-called additive hard-core interaction, namely, the one in which the distance of closest approach (denoted by σ_{ij}) between the centers of two interacting particles, one of species i and the other of species j, is the arithmetic mean of the diameters of both particles σ_i and σ_j, respectively. Apart from the initial impetus that took place in the 1960s, recently, interest in this kind of systems (in particular, mixtures of hard spheres) has experienced an increasing growth in connection with entropy driven phase transitions and the demixing problem. On the other hand, nonadditive hard-core mixtures, where the distance of closest approach between particles of different species is no longer the arithmetic mean referred to above, have received less attention, in spite of their in principle more versatility to deal with interesting aspects occurring in real systems (such as liquid-vapor equilibrium or fluid-fluid phase separation) and of their potential use as reference systems in perturbation calculations on the thermodynamic and structural properties of, say, Lennard-Jones mixtures. Nevertheless, the study of nonadditive systems goes back 50 years[1–3] and is still a rapidly developing and challenging problem.

As mentioned in the paper by Ballone *et al.*,[4] where the relevant references may be found, experimental work on alloys, aqueous electrolyte solutions, and molten salts suggests that heterocoordination and homocoordination may be interpreted in terms of excluded volume effects due to nonadditivity of the repulsive part of the intermolecular potential. In particular, positive nonadditivity leads naturally to demixing in hard-sphere mixtures, so that some of the experimental findings of phase separation in the above mentioned (real) systems may be accounted for by using a model of a binary mixture of (positive) nonadditive hard spheres. On the other hand, negative nonadditivity seems to account well for chemical short-range order in amorphous and liquid binary mixtures with preferred hetero-coordination.[5]

On the theoretical side, the first exact result on the equation of state (EOS) for a nonadditive mixture is that of a binary mixture of hard rods ($d=1$) restricted to nearest-neighbor interactions. Although it is usually attributed to Lebowitz and Zomick,[6] it was already implicit in earlier work by Prigogine and Lafleur[1] and by Kikuchi,[3] and even Lebowitz and Zomick point out that the thermodynamic functions of this system appear in the thesis presented in 1966 by C. C. Carter (cf. Ref. 9 in Ref. 6). Very recently, Corti and Bowles have rederived this result in an appendix of a paper,[7] where they also provide exact geometrical relationships for nonadditive mixtures (see also an alternative rederivation in Prof. Penrose's webpage[8]). It is also worth mentioning that in the paper by Kikuchi,[3] a proof is given that no phase transition may occur in a one-dimensional binary mixture irrespective of the form of the interaction potential, provided it is unbounded. The opposite limit of high spatial dimension has been considered by Carmesin *et al.*,[9] who showed that at sufficiently high density and with positive nonadditivity, a binary mixture of nonadditive hard hyperspheres decomposes into two coexisting phases.

[a]Electronic mail: andres@unex.es;
URL: http://www.unex.es/fisteor/andres/
[b]On sabbatical leave from Centro de Investigación en Energía, U.N.A.M., Temixco, Morelos 62580, México;
Electronic mail: malopez@servidor.unam.mx;
URL: http://miquiztli.cie.unam.mx/xml/tc/ft/mlh/
[c]Electronic mail: santos@unex.es;
URL: http://www.unex.es/fisteor/santos/sby

A very popular model of a nonadditive binary mixture with positive nonadditivity was introduced by Widom and Rowlinson in 1970.[10] This model is equivalent to a one-component penetrable sphere model. In the symmetric version of the model, referred to as the Widom–Rowlinson (WR) model, one has $\sigma_1=\sigma_2=0$ and $\sigma_{12}>0$. With this simplification Widom and Rowlinson derived exactly the EOS in the one-dimensional case, where it predicts no phase transition. For $d=3$ the model was solved in the mean-field approximation. In the same paper, but for the case of high asymmetry (i.e., when $\sigma_1\neq 0$, $\sigma_2=0$, and $d=3$), Widom and Rowlinson also determined an approximate condition for the spinodal curve. It is interesting to point out that this case of high asymmetry corresponds with the Asakura–Oosawa model,[2] often used to discuss polymer colloid mixtures and where the notion of a depletion potential was introduced. This model and refinements of the same have received a lot of attention (including fairly recent work) in connection with the demixing problem and the question of effective potentials.[11]

The impact of the WR model cannot be overemphasized as it has motivated a great amount of later work. A rigorous proof that a phase transition may exist in the WR model in $d=2$ was provided by Ruelle,[12] who also indicated that a similar procedure may be followed to prove the existence of a phase transition in the WR model in $d=3$ and higher dimensions. Frisch and Carlier[13] performed molecular dynamics simulation for a hard-square mixture in the WR limit and concluded that it presented a first-order phase transition. Melnyck *et al.*[14] obtained the first ten virial coefficients of the WR hard-sphere mixture in the Percus–Yevick (PY) approximation (the first five of which are exact), while Straley *et al.*[15] computed the virial coefficients of the WR model for oriented hard squares and hard cubes. Widom and Stillinger[16] generalized the scaled particle theory (SPT) for a pure fluid[17] to the case of the WR model in an arbitrary dimensionality and Guerrero *et al.*[18] exploited the equivalence of the penetrable sphere model and the WR model to obtain the direct and total correlation functions for the model where the Mayer function is a Gaussian and for the hard-sphere interaction in the mean field, PY, and hypernetted chain approximations. In the cases of $d=1$ and $d=3$, the WR model was solved in the PY approximation by Ahn and Lebowitz,[19] while the SPT was considered by Bergmann.[20] The latter theory for the WR model in two dimensions was addressed in an appendix of the paper by Tenne and Bergmann,[21] in which they examined the SPT for a nonadditive hard-disk binary mixture. Transport properties for the WR hard-sphere binary mixture were computed by Karkheck and Stell.[22] Later, Borgelt *et al.*[23] and Luo *et al.*[24] performed simulations on the hard-sphere WR mixture and found better agreement with mean-field results than with PY results. More recently, the same model has been the subject of investigations related to its universality class,[25] to the location of the critical point and the computation of the coexistence curve,[26] to the development of an integral equation theory that includes the first few terms in the density expansion of the direct correlation function into the closure approximation,[27] to the (partial) total and direct correlation functions[28] through accurate Monte Carlo simulations, and to the static and dynamic behavior near the consolute critical point obtained from molecular dynamics simulations.[29]

A theoretical approach that has been extensively used in connection with nonadditive hard-core mixtures is the SPT. Apart from the papers quoted above, Bergmann[30] has considered the SPT in one dimension and compared it with the exact solution. Tenne and Bergmann examined the SPT for $d=3$ both for positive nonadditivity[31] (where they computed the critical density and the critical nonadditivity) and negative nonadditivity.[32] Bearman and Mazo also considered the SPT for a symmetric binary mixture of nonadditive hard disks[33] and pointed out that the phase transition predicted by Tenne and Bergmann in Ref. 21 for negative nonadditivity was spurious. The same authors[34] introduced a simpler version of the SPT for $d=2$ and $d=3$ which is consistent with the SPT of additive mixtures in the appropriate limit but still presents some other difficulties. Some of these difficulties were addressed by Schaink,[35] who introduced an EOS for a binary mixture valid for small values of the nonadditivity. A comparison of SPT predictions and simulation data may be found in Ehrenberg *et al.*[36]

The use of computer simulation, both molecular dynamics (MD) and Monte Carlo (MC), as well as of the usual integral equation approach of liquid state theory or the perturbation theory (taking either a one-component system or a binary additive hard-core mixture as the reference system) has also contributed to the investigation of the properties of nonadditive hard-core mixtures. In the same paper where they presented the exact solution for the one-dimensional mixture, Lebowitz and Zomick[6] also gave the exact solution to the PY equation in $d=1$ and a partial solution to the PY equation in the three-dimensional case. A mathematical analysis of these two solutions was later given by Penrose and Lebowitz.[37] Perry and Silbert[38] also gave an approximate solution to the PY equation in $d=3$ which confirmed the earlier results of Lebowitz and Zomick. For equimolar and symmetric hard-sphere mixtures with negative nonadditivity, Nixon and Silbert[39] solved the PY equation, which they found to improve its agreement with simulation data as the negative nonadditivity increased. Equimolar symmetric binary mixtures have been studied by Gazzillo.[40–42] He has considered the PY approximation[40] and also other closures (the Martynov–Sarkisov,[43] the Ballone–Pastore–Galli-Gazzillo,[4] and the modified Verlet[41,42] closures). In Ref. 42 he also addressed a ternary mixture with negative nonadditivity that had been studied earlier through MD simulation by Schaink,[44] while he and his collaborators[4] were apparently the first to obtain simulation (MC) data for an asymmetric hard-sphere binary system. In studying binary nonadditive Lennard-Jones mixtures using the reference hypernetted chain (RHNC) approximation, Anta and Kahl[45] obtained the nonadditive hard-sphere bridge functions by solving the corresponding PY equation. Lomba *et al.*[46] used a generalized modified Verlet closure to study fluid-fluid phase separation in symmetric nonadditive hard-sphere mixtures, obtaining good agreement with their own MC simulation data for the phase diagram. Kahl *et al.*[47] studied a variety of symmetric binary mixtures of nonadditive hard spheres (both with posi-

tive and negative nonadditivity) by solving the Ornstein-Zernike equation with a modified hypernetted-chain-type closure. Recently, Sierra and Duda[48] considered the PY and Martynov-Sarkisov closures to study symmetric mixtures of nonadditive hard spheres adsorbed on a disordered hard-sphere matrix, while Duda *et al.*[49] used MC simulations to study fluid-fluid phase equilibria and interfacial properties of nonadditive binary hard-sphere mixtures adsorbed in a slit pore. The structure and the thermodynamics of nonadditive hard-sphere mixtures under confinement have also been the subject of a recent study by Pellicane *et al.*,[50] who used both integral equations and computer simulations.

Melnyck and Sawford[51] reported MD simulation data on a symmetric binary nonadditive hard-sphere mixture with positive nonadditivity and using perturbation theory derived an EOS for this kind of systems which they named MIX1. Such EOS was later extended to cope with asymmetric mixtures by Schaink and Hoheisel.[52] At about the same time as the Melnyck and Sawford calculations, Adams and McDonald[53] performed MC simulations on binary symmetric hard-sphere mixtures with negative nonadditivity. Later on, Dickinson[54] performed MD simulations on two equimolar nonadditive binary hard-disk mixtures. In 1989, Amar[55] computed the coexistence curve for the system studied in Ref. 51 using MC simulation. Hoheisel[56] studied a symmetric equimolar binary mixture of nonadditive soft spheres with (high) positive nonadditivity through MD and determined the critical density. Mountain and Harvey[57] conducted both MD and MC simulations on binary mixtures of nonadditive soft disks to study fluid-fluid coexistence. Rovere and Pastore[58] extended the work of Ref. 53 and obtained the coexistence curve of an asymmetric binary nonadditive hard-sphere mixture through MC simulation. Extensive MC computations on symmetric nonadditive hard-sphere binary mixtures have been provided by Jung *et al.*,[59–61] who have derived from them reasonably accurate (semiempirical) equations of state for these systems. Density functional theory has also been applied[62] to the computation of the excess free energy of an equimolar mixture of nonadditive hard disks. Finally, recently, Hamad has reported MD calculations for asymmetric nonadditive binary hard-sphere mixtures[63] and, together with some co-workers, also for binary hard-disk mixtures.[64] Fluid-fluid phase separation in a symmetric mixture of nonadditive hard spheres with positive nonadditivity and the phase behavior of nonadditive hard-core mixtures in two dimensions have been recently the subject of MC simulations by Saija *et al.*[65] and by Saija and Giaquinta,[66] respectively, while Góźdź[67] performed MC simulations to derive accurate results for the critical packing fraction at a few values of the nonadditivity parameter in the case of hard spheres. Castañeda-Priego *et al.*[68] studied depletion interactions in mixtures of nonadditive hard disks, Schmidt[69] generalized the fundamental measure density functional theory of hard spheres to binary mixtures of arbitrary positive and moderate negative nonadditivity, and Fantoni and Pastore[70] performed accurate MC simulations to check the local dependency assumption of the bridge functions of an equimolar nonadditive binary hard-sphere mixture. Fairly recently, Buhot[71] used a cluster algorithm to simulate and study phase separation in symmetric binary mixtures of nonadditive hard disks and hard spheres for various (large) nonadditivities including the limiting case of the WR model.

An alternative route to the derivation of the EOS of nonadditive hard-sphere mixtures that does not require the SPT, perturbation theory, the solution of integral equations, or simulation results relies on the knowledge of virial coefficients and on the use of exact statistical mechanical relationships. The so-called y expansion for hard particle fluids introduced by Barboy and Gelbart[72] is a prominent example of this approach. In the case of nonadditive hard-sphere mixtures, the Barboy–Gelbart EOS involves up to the exact third virial coefficients, whose analytical expressions are known.[73] On a different path, Hamad[74] has provided a theory for obtaining mixture properties from pure species equations of state. In the case of nonadditive hard-sphere mixtures, he invokes exact results pertaining to the contact values of the radial distribution functions,[75–77] as well as the knowledge of the exact second and third virial coefficients. He has also presented a similar approach for hard-disk mixtures in Refs. 64 and 78. A noteworthy aspect of Hamad's proposal is that, due to his use of the one-component radial distribution function as a starting point, it is geared essentially towards mixtures not very asymmetric in size. This proposal has been very recently used in connection with the development of a perturbation theory for fused sphere hard-chain fluids.[79]

Recently,[80,81] we have proposed an EOS for a multicomponent mixture of additive hard-core particles in d dimensions. This proposal shares with Hamad's approach[64,74,78] two aspects. On the one hand, it is expressed in terms of the pure species EOS and on the other it starts with a sensible ansatz on the functional form of the contact values of the radial distribution functions. The aim of this paper is to complement Hamad's approach in two different veins. The first one concerns dimensionality. Here we want to derive an EOS for a nonadditive hard-core mixture of an arbitrary number of components and for any value of d. The second one has to do with the fact that when the nonadditivity parameter vanishes we also want to recover our former proposal[80] for additive multicomponent hard-core mixtures. Our main concern is to try to keep a reasonable compromise between the simplicity of the proposal and its ability to deal also with highly asymmetric mixtures.

The paper is organized as follows. In Sec. II we provide general expressions for a multicomponent mixture of nonadditive hard spheres in d dimensions and some key background material (third virial coefficients, for which a simple expression for arbitrary dimensionality is proposed) for the later development. The exact solution in the case of a one-dimensional binary mixture as well as other interesting features of this system are presented in Appendix A. Section III contains a brief account of Hamad's proposal[64,76,77] for the contact values of the radial distribution functions and for the compressibility factor of the mixture. This is followed in Sec. IV by our own proposal, which shares with Hamad's a few features: the construction of the EOS via the contact values of the radial distribution functions, the dependence of the latter on the EOS of the one-component fluid, and the use

of the third virial coefficients. The results pertaining to special limiting cases are given in Appendix B. The analysis of the fourth, fifth, and sixth virial coefficients and of the compressibility factors in one, two, and three dimensions is carried out in Sec. V. The paper is closed in Sec. VI with further discussion and some concluding remarks.

II. THIRD VIRIAL COEFFICIENTS

A. General equations

Let us consider an N-component mixture of hard spheres in d dimensions. The hard core of the interaction between a sphere of species i and a sphere of species j is σ_{ij}. The diameter of a sphere of species i is $\sigma_{ii}=\sigma_i$. In general, $\sigma_{ij}=\frac{1}{2}(\sigma_i+\sigma_j)(1+\Delta_{ij})$, where $\Delta_{ij}\geqslant -1$ is a symmetric matrix with zero diagonal elements ($\Delta_{ii}=0$) that characterizes the degree of nonadditivity of the interactions. In the case of a binary mixture ($N=2$), the only nonadditivity parameter is $\Delta=\Delta_{12}=\Delta_{21}$. The compressibility factor of the mixture $Z\equiv p/\rho k_B T$, where ρ is the total number density, p is the pressure, T is the temperature, and k_B is the Boltzmann constant, can be exactly expressed in terms of the radial distribution functions at contact g_{ij} as

$$Z(\rho,\{x_k\},\{\sigma_{k\ell}\})=1+2^{d-1}v_d\rho\sum_{i,j=1}^{N}x_i x_j\sigma_{ij}^d \times g_{ij}(\rho,\{x_k\},\{\sigma_{k\ell}\}), \tag{1}$$

where $x_i=\rho_i/\rho$ is the mole fraction of species i, ρ_i is the partial number density of particles of species i, and $v_d=(\pi/4)^{d/2}/\Gamma(1+d/2)$ is the volume of a d-dimensional sphere of unit diameter. Although no general expression is known for $g_{ij}(\rho,\{x_k\},\{\sigma_{k\ell}\})\equiv g_{ij}(\rho)$, it can be expanded in a power series in density as

$$g_{ij}(\rho)=1+v_d\rho\sum_{k=1}^{N}x_k c_{k;ij}+(v_d\rho)^2\sum_{k,\ell=1}^{N}x_k x_\ell c_{k\ell;ij}+O(\rho^3). \tag{2}$$

The coefficients $c_{k;ij}$, $c_{k\ell;ij}$,... are independent of the composition of the mixture, but they are in general complicated nonlinear functions of the diameters σ_{ij}, σ_{ik}, σ_{jk}, $\sigma_{k\ell}$,.... Insertion of the expansion (2) into Eq. (1) yields the virial expansion of Z, namely,

$$Z(\rho)=1+\sum_{n=1}^{\infty}(v_d\rho)^n\overline{B}_{n+1}=1+v_d\rho\sum_{i,j=1}^{N}\overline{B}_{ij}x_i x_j+(v_d\rho)^2\sum_{i,j,k=1}^{N}\overline{B}_{ijk}x_i x_j x_k+(v_d\rho)^3\sum_{i,j,k,\ell=1}^{N}\overline{B}_{ijk\ell}x_i x_j x_k x_\ell+O(\rho^4). \tag{3}$$

Note that, for further convenience, we have introduced the coefficients $\overline{B}_n\equiv v_d^{-(n-1)}B_n$ where B_n are the usual virial coefficients. The composition-independent second, third, and fourth (barred) virial coefficients are given by

$$\overline{B}_{ij}=2^{d-1}\sigma_{ij}^d, \tag{4}$$

$$\overline{B}_{ijk}=\frac{2^{d-1}}{3}(c_{k;ij}\sigma_{ij}^d+c_{j;ik}\sigma_{ik}^d+c_{i;jk}\sigma_{jk}^d), \tag{5}$$

$$\overline{B}_{ijk\ell}=\frac{2^{d-1}}{6}(c_{k\ell;ij}\sigma_{ij}^d+c_{j\ell;ik}\sigma_{ik}^d+c_{i\ell;jk}\sigma_{jk}^d+c_{jk,i\ell}\sigma_{i\ell}^d+c_{ik,j\ell}\sigma_{j\ell}^d+c_{ij;k\ell}\sigma_{k\ell}^d). \tag{6}$$

This connection between the virial coefficients of the mixture and c's of the density expansion of the contact values of the radial distribution functions may be profitably used to devise sensible approximations.

For subsequent use in Secs. III and IV, it is convenient to consider the special case of a one-component fluid ($\sigma_{ij}=\sigma$) of packing fraction $y=v_d\rho\sigma^d$. In such a case, Eqs. (1) and (3) become

$$Z_{\text{pure}}(y)=1+2^{d-1}yg_{\text{pure}}(y)=1+\sum_{n=1}^{\infty}b_{n+1}y^n, \tag{7}$$

where $b_n=\overline{B}_n/\sigma^{(n-1)d}$ are the (reduced) virial coefficients of the one-component hard-sphere fluid. In particular, $b_2=2^{d-1}$.

B. The one-dimensional case

It is worth recalling that, as mentioned in Sec. I, in the case of a *binary* ($N=2$) one-dimensional ($d=1$) mixture with nearest-neighbor interactions only [which implies that $2\sigma_{12}\geqslant\max(\sigma_1,\sigma_2)$], the exact compressibility factor is known.[1,3,6–8] In Appendix A we provide a summary of the exact solution as well as some interesting properties of the same. In particular, the coefficients $c_{k;ij}$ for $d=1$ are

$$c_{1;11}=\sigma_1,\quad c_{2;11}=2\sigma_{12}-\sigma_1,\quad c_{1;12}=\sigma_1. \tag{8}$$

The remaining coefficients are obtained from Eq. (8) by the exchange $1\leftrightarrow 2$.

C. The three-dimensional case

In three dimensions, the first two terms of the exact density expansion of g_{ij} are known.[76] After a few simple manipulations one may derive from them the result

$$c_{k;ij}=\sigma_{k;ij}^3+\frac{3}{2}\frac{\sigma_{k;ij}^2}{\sigma_{ij}}\sigma_{i;jk}\sigma_{j;ik}, \tag{9}$$

where

$$\sigma_{k;ij}\equiv\sigma_{ik}+\sigma_{jk}-\sigma_{ij} \tag{10}$$

and it is understood that $\sigma_{k;ij}\geqslant 0$ for all sets ijk. Clearly, $\sigma_{i;ij}=\sigma_i$, $\sigma_{j;ij}=\sigma_j$, and, in case of additive hard spheres, $\sigma_{k;ij}=\sigma_k$. Note also that the quantities $\sigma_{k;ij}$ may be given a simple geometrical interpretation. Assume that we have three spheres of species i, j, and k aligned in the sequence ikj. In such a case, the distance of closest approach between the centers of spheres i and j is $\sigma_{ik}+\sigma_{jk}$. If the sphere of species k were not there, that distance would of course be σ_{ij}. Therefore, $\sigma_{k;ij}$ as given by Eq. (10) represents a kind of effective diameter of sphere k, as seen from the point of

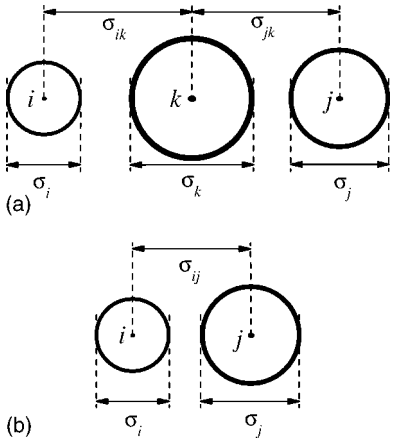

FIG. 1. (a) Three spheres of species i, j, and k in an aligned configuration. The smallest possible separation between spheres i and j is $\sigma_{ik}+\sigma_{jk}$. (b) When sphere k is removed, the smallest distance between i and j is σ_{ij}. Thus $\sigma_{k;ij}=\sigma_{ik}+\sigma_{jk}-\sigma_{ij}$ represents an effective diameter of sphere k as seen from the point of view of the pair ij. In the sketch we have assumed for simplicity that the nonadditivities are positive.

view of the interaction between spheres i and j. A schematic representation of this interpretation is provided in Fig. 1.

D. A generalization to *d* dimensions

It is tempting to extend Eqs. (8) and (9) to d dimensions as

$$c_{k;ij}=\sigma_{k;ij}^d+\left(\frac{b_3}{b_2}-1\right)\frac{\sigma_{k;ij}^{d-1}}{\sigma_{ij}}\sigma_{i;jk}\sigma_{j;ik}. \tag{11}$$

More specifically, for a binary mixture Eq. (11) yields

$$\begin{aligned} c_{1;11}&=\frac{b_3}{b_2}\sigma_1^d,\\ c_{2;11}&=(2\sigma_{12}-\sigma_1)^d+\left(\frac{b_3}{b_2}-1\right)\sigma_1(2\sigma_{12}-\sigma_1)^{d-1},\\ c_{1;12}&=\sigma_1^d+\left(\frac{b_3}{b_2}-1\right)(2\sigma_{12}-\sigma_1)\sigma_1^d/\sigma_{12}. \end{aligned} \tag{12}$$

Obviously, Eq. (12) reduces to Eq. (8) for $d=1$ ($b_2=b_3=1$), while Eq. (11) reduces to Eq. (9) for $d=3$ ($b_2=4$, $b_3=10$).

All of the above results are restricted to the situation $\sigma_{k;ij}\geqslant 0$ for any choice of i, j, and k, i.e., $2\sigma_{12}\geqslant\max(\sigma_1,\sigma_2)$ in the binary case. This excludes the possibility of dealing with mixtures with extremely high negative nonadditivity in which one sphere of species k might "fit in" between two spheres of species i and j in contact. Since for $d=3$ and $N=2$ the coefficients $c_{k;ij}$ are also known for such mixtures,[74] we may extend our proposal to deal with these cases. If $N=2$, one has specifically

$$\begin{aligned} c_{1;11}&=\frac{b_3}{b_2}\sigma_1^d,\quad c_{2;11}=\hat{\sigma}_2^d+\left(\frac{b_3}{b_2}-1\right)\sigma_1\hat{\sigma}_2^{d-1},\\ c_{1;12}&=(2\sigma_{12}-\hat{\sigma}_2)^d+\left(\frac{b_3}{b_2}-1\right)\hat{\sigma}_2\sigma_1^d/\sigma_{12}, \end{aligned} \tag{13}$$

where we have defined

$$\hat{\sigma}_2=\max(2\sigma_{12}-\sigma_1,0). \tag{14}$$

With such an extension, we recover the exact values of $c_{k;ij}$ for a binary mixture of hard spheres ($d=3$), even if $\sigma_1>2\sigma_{12}$ or $\sigma_2>2\sigma_{12}$. We emphasize that Eqs. (11)–(14) for $d\neq 1$ and $d\neq 3$ are new.

E. The two-dimensional case

While Eq. (13) is exact for $d=1$ and $d=3$, it is only approximate for $d=2$. For that dimensionality, the exact result has been derived by Al-Naafa *et al.*[64] After some algebra (and the correction of some typos), the coefficients $c_{k;ij}$ can be written as

$$\begin{aligned} c_{1;11}&=\frac{b_3}{2}\sigma_1^2,\quad c_{2;11}=\frac{b_3}{2}\sigma_1^2F(\sigma_{12}/\sigma_1),\\ c_{1;12}&=\frac{b_3}{2}\sigma_1^2G(\sigma_{12}/\sigma_1), \end{aligned} \tag{15}$$

where $b_3=16/3-(4\sqrt{3}/\pi)\simeq 3.1280$ and the functions $F(s)$ and $G(s)$ are given by

$$F(s)=\begin{cases}\dfrac{4}{\pi b_3}\left(4s^2\cos^{-1}\dfrac{1}{2s}-\sqrt{4s^2-1}\right), & s\geqslant\dfrac{1}{2}\\ 0, \quad 0\leqslant s\leqslant\frac{1}{2}, & \end{cases} \tag{16}$$

$$G(s)=\begin{cases}\dfrac{4}{\pi b_3}[2\pi s^2-2(2s^2-1)\cos^{-1}\dfrac{1}{2s}\\ -\sqrt{4s^2-1}], \quad s\geqslant\frac{1}{2}\\ \dfrac{8}{b_3}s^2, \quad 0\leqslant s\leqslant\dfrac{1}{2}. \end{cases} \tag{17}$$

Some special values of $F(s)$ and $G(s)$ are

$$F(1)=G(1)=1, \tag{18}$$

$$F(1/2)=0,\quad G(1/2)=\frac{2}{b_3}, \tag{19}$$

$$\lim_{s\to\infty}s^{-2}F(s)=\frac{8}{b_3},\quad \lim_{s\to\infty}G(s)=\frac{4}{b_3}. \tag{20}$$

For a symmetric mixture ($\sigma_1=\sigma_2$), the value $s=\sigma_{12}/\sigma_1=1$ corresponds to the one-component case, $s=\sigma_{12}/\sigma_1=\frac{1}{2}$ corresponds to the threshold value of negative nonadditivity (i.e., $2\sigma_{12}=\sigma_1=\sigma_2$ or $\Delta=-\frac{1}{2}$), and the limit $s=\sigma_{12}/\sigma_1\to\infty$ represents an infinitely large positive nonadditivity (WR model).

Equation (13) with $d=2$ can be recast into the form (15), except that the functions $F(s)$ and $G(s)$ are approximated by

$$F_{\text{app}}(s)=\begin{cases}\dfrac{1}{b_3}(2s-1)(4s+b_3-4), & s\geqslant\dfrac{1}{2}\\ 0, \quad 0\leqslant s\leqslant\frac{1}{2}, & \end{cases} \tag{21}$$

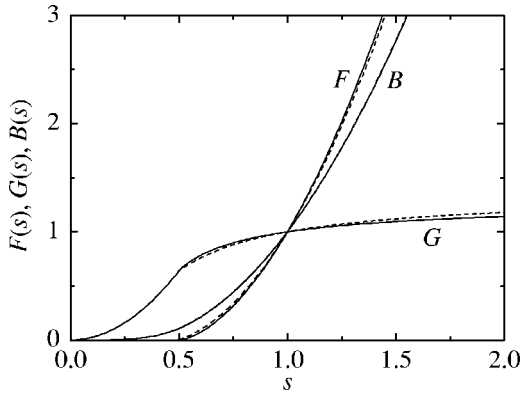

FIG. 2. Plot of the functions $F(s)$, $G(s)$, and $B(s)$. The solid lines are the exact functions (16), (17), and (25), while the dashed lines are our approximations (21), (22), and (26). Note that $B(s)$ and $B_{\text{app}}(s)$ are practically indistinguishable.

$$G_{\text{app}}(s)=\begin{cases}\dfrac{2}{b_3}\left(b_3-1-\dfrac{b_3-2}{2s}\right), & s\geqslant\dfrac{1}{2}\\ \dfrac{8}{b_3}s^2, & 0\leqslant s\leqslant\dfrac{1}{2}.\end{cases}\tag{22}$$

This approximation verifies the properties (19) and (20), except that now $\lim_{s\to\infty}G_{\text{app}}(s)=2(b_3-1)/b_3$, which is about 6% higher than the exact value. Figure 2 shows that Eqs. (21) and (22) constitute an excellent approximation to the exact expressions (16) and (17), especially for small or moderate values of s.

The third virial coefficients $\overline{B}_{ijk}$ for a two-dimensional binary mixture as given by Eq. (5) may be cast into the form

$$\overline{B}_{111}=2c_{1;11}\sigma_1^2=b_3\sigma_1^4,\tag{23}$$

$$\overline{B}_{112}=\tfrac{2}{3}(c_{2;11}\sigma_1^2+2c_{1;12}\sigma_{12}^2)=b_3\sigma_1^4B(\sigma_{12}/\sigma_1),\tag{24}$$

and similar expressions for $\overline{B}_{222}$ and $\overline{B}_{221}$, obtained from the former by the exchange of indices 1 and 2. Here,

$$B(s)\equiv\tfrac{1}{3}F(s)+\tfrac{2}{3}s^2G(s)$$
$$=\begin{cases}\dfrac{4}{3\pi b_3}[4\pi s^4-8s^2(s^2-1)\cos^{-1}\dfrac{1}{2s}\\ \qquad -(2s^2+1)\sqrt{4s^2-1}], & s\geqslant\dfrac{1}{2}\\ \dfrac{16}{3b_3}s^4, & 0\leqslant s\leqslant\dfrac{1}{2}.\end{cases}\tag{25}$$

Using Eqs. (21) and (22) our approximation yields for $B_{\text{app}}(s)$ the polynomial

$$B_{\text{app}}(s)=\begin{cases}\dfrac{1}{3b_3}[4(s-1)^2+b_3(4s^2-1)], & s\geqslant\dfrac{1}{2}\\ \dfrac{16}{3b_3}s^4, & 0\leqslant s\leqslant\dfrac{1}{2}.\end{cases}\tag{26}$$

As also seen in Fig. 2, Eq. (26) is practically indistinguishable from the exact $B(s)$, so that the (small) discrepancies in $F_{\text{app}}(s)$ and $G_{\text{app}}(s)$ with respect to the actual $F(s)$ and $G(s)$ almost entirely compensate. Therefore, it seems that it is not unreasonable to use Eqs. (11)–(14) for all d.

III. HAMAD'S PROPOSAL FOR THE EQUATION OF STATE

Our goal is to derive an (approximate) EOS for a multicomponent mixture of d-dimensional nonadditive hard spheres. Clearly, this may be achieved if values for the g_{ij} are provided. But before we engage in this task, let us recall in this section a previous simple proposal by Hamad.

Hamad[64,76,77] has proposed a simple and accurate approximation for the contact values of the radial distribution functions which takes the same form in both $d=2$ and $d=3$. Generalized to arbitrary dimensionality d and in the notation of this paper it reads

$$g_{ij}^{\text{H}}(\rho)=g_{\text{pure}}(\eta X_{ij}),\quad X_{ij}=\frac{b_2}{b_3}\frac{\sum_k x_k c_{k;ij}}{\langle\sigma^d\rangle}.\tag{27}$$

Here, $\eta\equiv v_d\rho\langle\sigma^d\rangle$ is the packing fraction of the mixture, with $\langle\sigma^m\rangle=\sum_{i=1}^N x_i\sigma_i^m$.

By construction, the approximation (27) is correct to first order in the density (third virial coefficient). Inserting the approximation (27) into Eq. (1), we obtain the (generalized) d-dimensional Hamad EOS,

$$Z^{\text{H}}(\rho)=1+\frac{2^{d-1}\eta}{\langle\sigma^d\rangle}\sum_{i,j}x_ix_j\sigma_{ij}^d g_{\text{pure}}(\eta X_{ij})$$
$$=1+\sum_{i,j}\frac{x_ix_j\sigma_{ij}^d}{\langle\sigma^d\rangle}\left[\frac{Z_{\text{pure}}(\eta X_{ij})-1}{X_{ij}}\right].\tag{28}$$

So far, the one-component function $Z_{\text{pure}}(y)$ remains free. It should be emphasized that, except for $d=2$ and $d=3$, the EOS given by Eq. (28) has been neither introduced nor used before.

The Helmholtz free energy per particle of a mixture, $a(\rho)$, is given by

$$\frac{a(\rho)}{k_BT}=-1+\sum_{i=1}^N x_i\ln(\rho_i\lambda_i^d)+\int_0^\rho\frac{d\rho'}{\rho'}[Z(\rho')-1],\tag{29}$$

where λ_i is the thermal de Broglie wavelength of species i. According to Hamad's approximation (28),

$$\frac{a^{\text{H}}(\rho)}{k_BT}=-1+\sum_i x_i\ln(\rho_i\lambda_i^d)$$
$$+\sum_{i,j}\frac{x_ix_j\sigma_{ij}^d}{\langle\sigma^d\rangle X_{ij}}\frac{a_{\text{pure}}^{\text{ex}}(\eta X_{ij})}{k_BT},\tag{30}$$

where $a_{\text{pure}}^{\text{ex}}(y)$ is the excess Helmholtz free energy per particle of the pure fluid.

IV. OUR PROPOSAL

In 1999 we proposed an EOS for a multicomponent mixture of *additive* hard spheres in d dimensions[80] which was based on an ansatz related to the contact values of the radial distribution functions. One may express this ansatz as

$$g_{ij}^{\mathrm{SYH}}(\rho)=\frac{1}{1-\eta}+\left[g_{\mathrm{pure}}(\eta)-\frac{1}{1-\eta}\right]z_{ij}, \tag{31}$$

where

$$z_{ij}=\frac{\langle\sigma^{d-1}\rangle\sigma_i\sigma_j}{\langle\sigma^d\rangle\sigma_{ij}} \quad \text{(additive spheres)} \tag{32}$$

is a parameter that is independent of density but depends on the composition and diameters of the mixture.

The idea is now to generalize the ansatz given by Eq. (31) to the nonadditive case. As the simplest possible extension, we keep the structure of Eq. (31) but determine the parameters z_{ij} as to reproduce Eq. (2) to first order in the density. The result is readily found to be

$$z_{ij}=\left(\frac{b_3}{b_2}-1\right)^{-1}\left(\frac{\Sigma_k x_k c_{k;ij}}{\langle\sigma^d\rangle}-1\right). \tag{33}$$

The following relationship between z_{ij} and X_{ij} exists:

$$z_{ij}=\frac{b_3X_{ij}-b_2}{b_3-b_2}, \quad X_{ij}=z_{ij}+\frac{b_2}{b_3}(1-z_{ij}). \tag{34}$$

The ansatz (31) supplemented by Eq. (33) is, by construction, accurate for densities low enough as to justify the linear approximation $g_{ij}\approx 1+v_d\rho\Sigma_k x_k c_{k;ij}$. On the other hand, the limitations of this truncated expansion for moderate and large densities are compensated by the use of g_{pure}. Of course, $g_{ij}=g_{\mathrm{pure}}$ in the special case where all the diameters are identical ($\sigma_{k\ell}=\sigma$), since then $c_{k;ij}=(b_3/b_2)\sigma^d$ and $z_{ij}=1$. All these comments apply to Hamad's prescription (27) as well. On the other hand, Eq. (31) is consistent, but Eq. (27) is not, with the case of an additive mixture in which one of the species, say $i=1$, is made of point particles, so that $g_{11}=(1-\eta)^{-1}$.

When Eqs. (31) and (33) are inserted into Eq. (1) one gets

$$Z^{\mathrm{SYH}}(\rho)=1+\frac{\eta}{1-\eta}\frac{b_3\langle\sigma^d\rangle\overline{B}_2-b_2\overline{B}_3}{(b_3-b_2)\langle\sigma^d\rangle^2}+[Z_{\mathrm{pure}}(\eta)-1]\frac{\overline{B}_3-\langle\sigma^d\rangle\overline{B}_2}{(b_3-b_2)\langle\sigma^d\rangle^2}. \tag{35}$$

Equation (35) is the main result of this paper. As in Eq. (28), the EOS of the mixture is expressed in terms of that of the one-component system. On the other hand, the density dependence in the EOS (35) is simpler: $Z(\rho)-1$ is expressed as a linear combination of $\eta/(1-\eta)$ and $Z_{\mathrm{pure}}(\eta)-1$, with coefficients such that the second and third virial coefficients are reproduced. Again, Eq. (35) is accurate for sufficiently low densities, while the limitations of the truncated expansion for moderate and large densities are compensated by the use of the EOS of the pure fluid.

In the approximation (35), the Helmholtz free energy per particle is

$$\frac{a^{\mathrm{SYH}}(\rho)}{k_BT}=-1+\sum_i x_i\ln(\rho_i\lambda_i^d)-\ln(1-\eta)+\frac{b_3\langle\sigma^d\rangle\overline{B}_2-b_2\overline{B}_3}{(b_3-b_2)\langle\sigma^d\rangle^2}+\frac{a_{\mathrm{pure}}^{\mathrm{ex}}(\eta)}{k_BT}\frac{\overline{B}_3-\langle\sigma^d\rangle\overline{B}_2}{(b_3-b_2)\langle\sigma^d\rangle^2}. \tag{36}$$

In principle, to compute $\overline{B}_3$, one should use the exact coefficients $c_{k;ij}$. However, since to the best of our knowledge they are only known for $d\leqslant 3$ and we want our proposal to be explicit for any d, we can make use of our approximation for them, Eq. (11). Therefore, with this proviso we get

$$z_{ij}=\left(\frac{b_3}{b_2}-1\right)^{-1}\left(\frac{\Sigma_k x_k\sigma_{k;ij}^d}{\langle\sigma^d\rangle}-1\right)+\frac{\Sigma_k x_k\sigma_{k;ij}^{d-1}\sigma_{i;jk}\sigma_{j;ik}}{\langle\sigma^d\rangle\sigma_{ij}}. \tag{37}$$

In the additive case ($\sigma_{k;ij}\to\sigma_k$), Eq. (37) reduces to Eq. (32). Note that both for $d=1$ and $d=3$ there is no difference in the resulting compressibility factor because Eq. (11) yields the exact result. On the other hand, for other d, use of Eq. (37) also leads to Eq. (35), but with an approximate rather than the exact value for the third virial coefficient.

V. RESULTS

Once we have derived our approximation for the EOS of the mixture, Eq. (35), it is interesting to examine its performance. And since Hamad has carried out a comparison between his proposal, Eq. (28), and previous ones,[64,74,76,77] finding in general that it performs better, we will concentrate here on comparing the results obtained either through Hamad's prescription or through ours (in this regard see also Appendix B). Such comparison seems in order in view of the fact that both proposals share many aspects such as the construction of the EOS via the contact values of the radial distribution functions, its dependence on the EOS of the one-component fluid (more specifically on Z_{pure}, which remains to be chosen freely), and the use of the third virial coefficients. Also, although Hamad's proposal is specific for $d=2$ and $d=3$ and we have extended it to arbitrary d, they maintain the same form in every dimensionality. Specifically, we will focus on the fourth and higher virial coefficients and on the compressibility factor. To our knowledge, and with the exception of the one-dimensional case, in which they are known exactly, values of the former are rather scarce[82,83] and refer exclusively to nonadditive hard spheres ($d=3$).

A. Fourth and higher virial coefficients

From Eq. (35) it is easy to get an approximate expression for the nth virial coefficient:

$$\overline{B}_n^{\mathrm{SYH}}=\frac{b_n-b_2}{b_3-b_2}\langle\sigma^d\rangle^{n-3}\overline{B}_3-\frac{b_n-b_3}{b_3-b_2}\langle\sigma^d\rangle^{n-2}\overline{B}_2. \tag{38}$$

In particular, the composition independent fourth virial coefficients are given by

$$\overline{B}_{ijk\ell}^{\mathrm{SYH}}=\frac{b_4-b_2}{4(b_3-b_2)}(\sigma_i^d\overline{B}_{jk\ell}+\sigma_j^d\overline{B}_{ik\ell}+\sigma_k^d\overline{B}_{ij\ell}+\sigma_\ell^d\overline{B}_{ijk})$$
$$-\frac{b_4-b_3}{6(b_3-b_2)}(\sigma_i^d\sigma_j^d\overline{B}_{k\ell}+\sigma_i^d\sigma_k^d\overline{B}_{j\ell}+\sigma_i^d\sigma_\ell^d\overline{B}_{jk}$$
$$+\sigma_j^d\sigma_k^d\overline{B}_{i\ell}+\sigma_j^d\sigma_\ell^d\overline{B}_{ik}+\sigma_k^d\sigma_\ell^d\overline{B}_{ij}). \quad (39)$$

In the case of Hamad's approximation, Eq. (28), one has

$$\overline{B}_n^{\mathrm{H}}=b_n\langle\sigma^d\rangle^{n-2}\sum_{i,j}x_ix_j\sigma_{ij}^dX_{ij}^{n-2}, \quad (40)$$

$$\overline{B}_{ijk\ell}^{\mathrm{H}}=\frac{b_4b_2^2}{6b_3^2}(\sigma_{ij}^dc_{k;ij}c_{\ell;ij}+\sigma_{ik}^dc_{j;ik}c_{\ell;ik}+\sigma_{i\ell}^dc_{j;i\ell}c_{k;i\ell}$$
$$+\sigma_{jk}^dc_{i;jk}c_{\ell;jk}+\sigma_{j\ell}^dc_{i;j\ell}c_{k;j\ell}+\sigma_{k\ell}^dc_{i;k\ell}c_{j;k\ell}). \quad (41)$$

In the special case of binary and symmetric $[\sigma_1=\sigma_2=\sigma,\sigma_{12}=\sigma(1+\Delta)]$ three-dimensional mixtures, Eqs. (39) and (41) yield

$$\overline{B}_{1112}^{\mathrm{SYH}}/\sigma^9=b_4(1+4\Delta+\tfrac{11}{2}\Delta^2+\tfrac{7}{3}\Delta^3)$$
$$-\Delta(10+16\Delta+\tfrac{22}{3}\Delta^2), \quad (42)$$

$$\overline{B}_{1122}^{\mathrm{SYH}}/\sigma^9=b_4(1+\tfrac{48}{9}\Delta+\tfrac{22}{3}\Delta^2+\tfrac{28}{9}\Delta^3)$$
$$-\tfrac{8}{9}\Delta(15+24\Delta+11\Delta^2), \quad (43)$$

$$\overline{B}_{1112}^{\mathrm{H}}/\sigma^9=b_4(1+\tfrac{9}{2}\Delta+\tfrac{162}{25}\Delta^2+\tfrac{144}{50}\Delta^3), \quad (44)$$

$$\overline{B}_{1122}^{\mathrm{H}}/\sigma^9=b_4(1+6\Delta+\tfrac{408}{25}\Delta^2+\tfrac{672}{25}\Delta^3+\tfrac{688}{25}\Delta^4$$
$$+\tfrac{384}{25}\Delta^5+\tfrac{256}{75}\Delta^6), \quad (45)$$

where $b_4=18.364\,77$ and we have assumed that $\Delta\geqslant-\frac{1}{2}$. The two coefficients $\overline{B}_{1112}$ and $\overline{B}_{1122}$ have been evaluated numerically by Saija *et al.*[82] Figure 3 compares the numerical data for $\overline{B}_{1112}$ and $\overline{B}_{1122}$ with the approximations (42)–(45). We observe that Hamad's approximation for $\overline{B}_{1112}$ gives an excellent agreement, while ours is only qualitatively correct. On the other hand, for $\overline{B}_{1122}$ both approximations are inaccurate for large positive nonadditivities. In any case, $\overline{B}_{1122}^{\mathrm{SYH}}$ is slightly better than $\overline{B}_{1122}^{\mathrm{H}}$ for $0<\Delta\lesssim0.3$.

Figure 4 shows, also for a symmetric binary mixture of nonadditive hard spheres, B_4/B_2^3 as a function of the mole fraction x_1 for $\Delta=-0.3$ and $\Delta=0.3$, and the corresponding simulation results. We observe that Hamad's approximation is better for $\Delta=-0.3$, while ours is better for $\Delta=0.3$.

As far as we know, the only report of virial coefficients beyond the third for the case of an asymmetric nonadditive hard-sphere mixture is due to Vlasov and Masters.[83] They have computed up to the sixth virial coefficient for a binary mixture of nonadditive hard spheres of size ratio 0.1 and a positive nonadditivity $\Delta=0.1$, and up to the seventh virial coefficient for a binary (additive) hard-sphere mixture of the same size ratio. In Fig. 5 we present a comparison of the results for the composition dependence of the ratio of virial coefficients B_n/B_2^{n-1} $(n=4,5,6)$ in the case of a binary mixture of size ratio $\sigma_2/\sigma_1=0.1$ and two nonadditivities ($\Delta=0,\ 0.1$) given by Vlasov and Masters[83] with the results that follow from Hamad's prescription and from our proposal. The overall superiority of our proposal in this case is apparent and more noticeable for the positive nonadditivity and

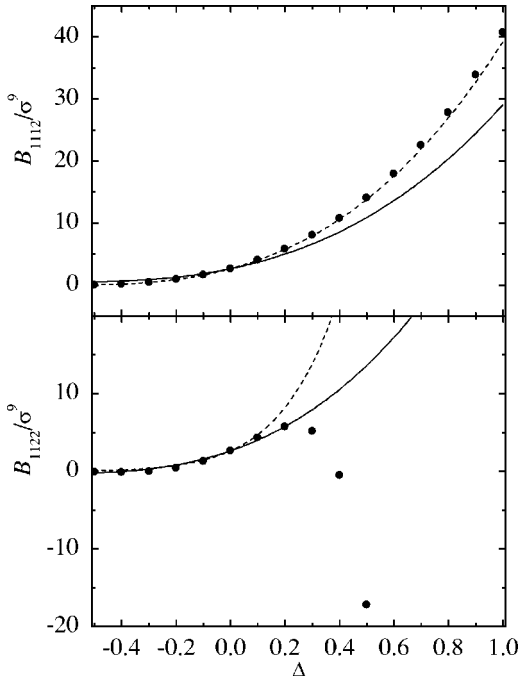

FIG. 3. Plots of $B_{1112}/\sigma^9=(\pi/6)^3\overline{B}_{1112}/\sigma^9$ and $B_{1122}/\sigma^9=(\pi/6)^3\overline{B}_{1122}/\sigma^9$ vs Δ for a symmetric three-dimensional binary mixture. Circles, exact values (Ref. 82); solid lines, Eqs. (42) and (43) (present approach); dashed lines, Eqs. (44) and (45) (Hamad's result).

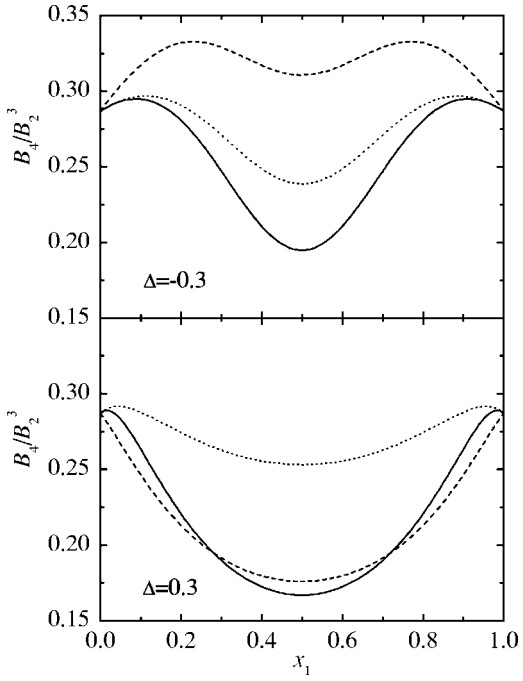

FIG. 4. Plot of B_4/B_2^3 vs x_1 for a symmetric three-dimensional binary mixture with $\Delta=-0.3$ and $\Delta=0.3$. Solid lines, exact values (Ref. 82); dashed line, Eq. (38) (present approach); dotted line, Eq. (40) (Hamad's result).

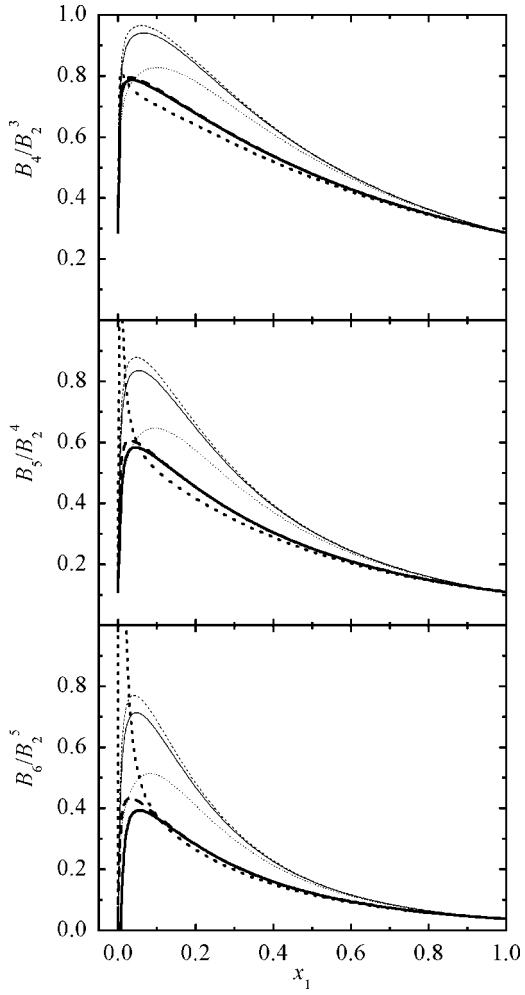

FIG. 5. Plot of B_n/B_2^{n-1} vs x_1 $(n=4,5,6)$ for an asymmetric three-dimensional binary mixture with $\sigma_2/\sigma_1=0.1$ and $\Delta=0$ (thin lines) and $\Delta=0.1$ (thick lines). Solid lines, exact values (Ref. 83); dashed lines, Eq. (38) (present approach); dotted lines, Eq. (40) (Hamad's result).

when n increases. Nevertheless, the negative values of the sixth virial coefficient for the small region around $x=0$ that are obtained with the simulation, not shown in the figure, are not captured by either proposal.

B. Compressibility factor

Apart from the virial coefficients, the most important tests concern the compressibility factor itself. In view of the big number of parameters in these systems, one has to make a judicious choice such that the main features of the results may be illustrated. In this section we provide a representative set of data for different dimensionalities that will hopefully cater for the above requirement.

1. Rods (d=1)

In the case $d=1$, one has $Z_{\text{pure}}(y)=1/(1-y)$ and $b_n=1$ for all n, so that our proposal (35) is ill defined. To save that singularity and with the aim of preserving the scaling property of the exact solution (see Appendix A), let us write

$$Z_{\text{pure}}(y)=\frac{1}{1-y}+\epsilon\left(\frac{y}{1-y}\right)^2, \quad b_3=1+\epsilon, \tag{46}$$

and set $\epsilon\to 0$ at the end of the calculations. In that case, replacement into Eq. (35) gives

$$Z^{\text{SYH}}(\rho)=1+\frac{\eta}{1-\eta}\frac{1}{\langle\sigma\rangle^2}\left[\langle\sigma\rangle\overline{B}_2+\frac{\eta}{1-\eta}(\overline{B}_3-\langle\sigma\rangle\overline{B}_2)\right], \tag{47}$$

which, for a binary mixture, becomes

$$Z^{\text{SYH}}(\rho)=\frac{1}{1-\eta}\left(1+x_1x_2\frac{\sigma_1+\sigma_2}{\langle\sigma\rangle}\frac{\eta}{1-\eta}\Delta\right). \tag{48}$$

Note that Eq. (48) is equivalent to a series expansion of the exact solution in powers of Δ truncated in the linear term. In fact, in view of Eqs. (A5)–(A7), it is exact up to order $O(\Delta^2)$. Also, it is important to point out that Eqs. (47) and (48) hold regardless of the value of ϵ, so the limit $\epsilon\to 0$ is not needed.

As for Hamad's approximation, we would have

$$X_{11}=1+\frac{\sigma_1+\sigma_2}{\langle\sigma\rangle}x_2\Delta, \quad X_{12}=1, \tag{49}$$

and the similar result for X_{22} obtained from X_{11} in Eq. (49) with the usual replacement $1\leftrightarrow 2$. After some algebra, one finds

$$Z^{\text{H}}=\frac{1}{1-\eta}\left\{1+x_1x_2\frac{\sigma_1+\sigma_2}{\langle\sigma\rangle}\times\eta\left[1+\eta\left(\frac{x_1\sigma_1/\langle\sigma\rangle}{1-\eta\left(1+\frac{\sigma_1+\sigma_2}{\langle\sigma\rangle}x_2\Delta\right)}+\frac{x_2\sigma_2/\langle\sigma\rangle}{1-\eta\left(1+\frac{\sigma_1+\sigma_2}{\langle\sigma\rangle}x_1\Delta\right)}\right)\right]\Delta\right\}. \tag{50}$$

We remark that Eq. (50) is exact to first order in Δ.

A comparison of the exact compressibility factor with our approximation (48) and Hamad's approximation (50) indicates that Eq. (48), being far simpler than Eq. (50), is better than the latter for $\Delta>0$, both approaches being comparably good for $\Delta<0$. This is illustrated in Fig. 6, where we display the exact Z as a function of the nonadditivity parameter for a symmetric $(\sigma_2/\sigma_1=1)$ and an asymmetric $(\sigma_2/\sigma_1=2)$ binary mixture of the same packing fraction $\eta=0.5$, and mole fraction $x_1=0.25$, together with the two theoretical approximations.

2. Disks (d=2)

It seems natural to begin with the case of symmetric binary mixtures, i.e., mixtures where $\sigma_1=\sigma_2$, and to investigate the effect of nonadditivity. Representative results in this respect for an equimolar symmetric binary mixture of nonadditive hard disks are displayed in the upper panel of Fig. 7, where we have plotted Z as a function of the nonadditivity parameter Δ at a packing fraction $\eta=0.4$. A similar plot of Z versus Δ is presented in the lower panel of Fig. 7, but in this case for an equimolar asymmetric mixture $(\sigma_2/\sigma_1=3)$ at the same packing fraction $\eta=0.4$.

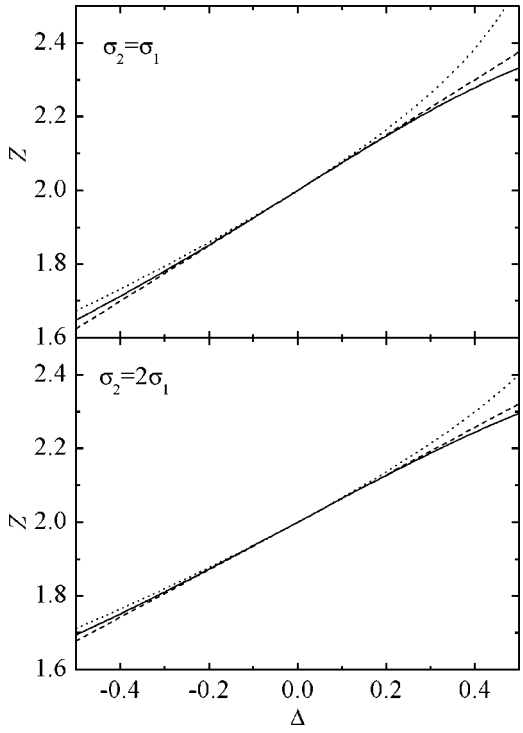

FIG. 6. Compressibility factor Z as a function of Δ for a symmetric mixture of nonadditive hard rods with $x_1=0.25$ at a packing fraction $\eta=0.5$ (upper panel) and for an asymmetric mixture with $x_1=0.25$ and $\sigma_2/\sigma_1=2$ at $\eta=0.5$ (lower panel). Solid lines, exact; dashed lines, Eq. (48) (present approach); dotted lines, Eq. (50) (Hamad's result).

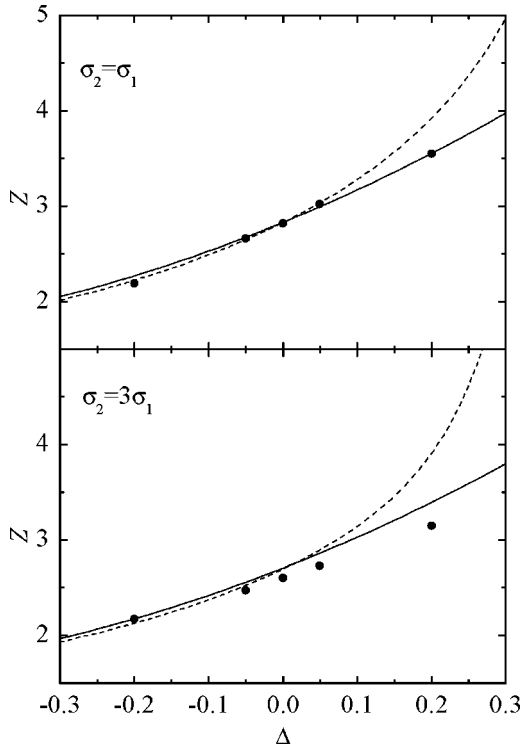

FIG. 7. Plot of the compressibility factor vs the nonadditivity parameter Δ for an equimolar symmetric binary mixture of nonadditive hard disks at a packing fraction $\eta=0.4$ (upper panel) and for an equimolar asymmetric mixture with $\sigma_2/\sigma_1=3$ at $\eta=0.4$ (lower panel). The solid lines are our proposal, Eq. (35), and the dashed lines are Hamad's proposal, Eq. (28). The circles are results from molecular dynamics simulations (Ref. 64).

The size ratio dependence of the compressibility factor is displayed in Figs. 8 and 9 for various combinations of mole fraction x_1, nonadditivity parameter Δ, and packing fraction η.

Although in the paper by Al-Naafa *et al.*[64] they evaluated Z^{H} by taking for Z_{pure} the one that follows from our own simple EOS for the hard-disk fluid,[84] in Figs. 7–9 we have considered for both proposals perhaps the most accurate EOS available nowadays, namely, the one due to Luding,[85]

$$Z_{\mathrm{pure}}^{\mathrm{Luding}}(y)=\frac{1+y^2/8}{(1-y)^2}-\frac{y^4}{64(1-y)^4}. \tag{51}$$

Once again we find that the trend observed in $d=1$ is also present in the case $d=2$, namely, that in general our proposal performs better than Hamad's, except for negative Δ. It is worth recalling here that Hamad's EOS includes the *exact* third virial coefficient, Eqs. (23)–(25), while ours makes use of the approximation embodied by Eq. (26).

3. Spheres (d=3)

We proceed here as in the case of $d=2$. Figure 10 shows Z as a function of Δ for a symmetric binary mixture of nonadditive hard spheres at the packing fraction $\eta=\pi/30\simeq 0.105$ and for $x_1=0.1$ and $x_1=0.5$. Here, as in all the rest of the calculations for hard spheres, Z_{pure} is the one corresponding to the Carnahan–Starling–Kolafa (CSK) EOS,[86]

$$Z_{\mathrm{pure}}^{\mathrm{CSK}}(y)=\frac{1+y+y^2-2y^3(1+y)/3}{(1-y)^3}. \tag{52}$$

In Fig. 11 we present a plot of Z versus Δ, but in this case for an equimolar asymmetric nonadditive hard-sphere mixture with $\sigma_2/\sigma_1=3$ at the packing fraction $\eta=0.5$. Finally, Fig. 12 is a plot of Z as a function of the size ratio for different values of x_1, Δ, and density. Once more these figures indicate that our proposal in the case of $d=3$ is superior to Hamad's, save for negative nonadditivity.

VI. CONCLUDING REMARKS

In this paper we have introduced a new proposal for the EOS of a multicomponent mixture of d-dimensional nonadditive hard spheres. This proposal is an immediate generalization of the one (rather accurate) we developed for additive hard spheres to which it immediately reduces if the nonadditivity parameters are set equal to zero. A general prescription for the d-dimensional composition-independent third virial coefficients of nonadditive hard-sphere mixtures has also been introduced. It is exact for $d=1$ and $d=3$ and does a very good job also for $d=2$. In the absence of exact results or simulation data for other dimensionalities, its merits in this respect remain to be evaluated.

Our proposal for the EOS involves providing (sensible) approximations for the contact values of the radial distribution functions that fulfill a few simple requirements. On the one hand, they reduce to the pure component value g_{pure} in the appropriate limit and also comply with the limit in which one of the species is made of point particles that do not occupy volume. On the other hand, they yield the exact g_{ij} to

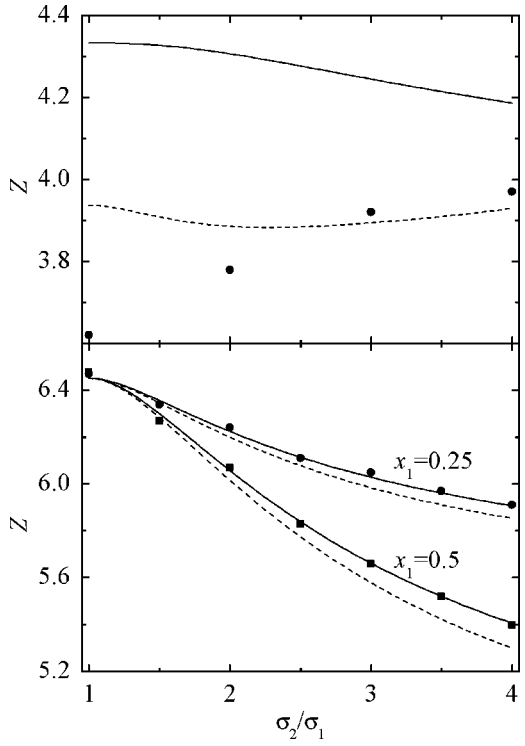

FIG. 8. Plot of the compressibility factor vs the size ratio σ_2/σ_1 for an equimolar binary mixture of nonadditive hard disks with $\Delta=-0.2$ at $\eta=0.6$ (upper panel) and for two binary additive hard-disk mixtures ($\Delta=0$) at $\eta=0.6$ (lower panel). The solid lines are our proposal, Eq. (35), and the dashed lines are Hamad's proposal, Eq. (28). The symbols are results from molecular dynamics simulations (Ref. 64).

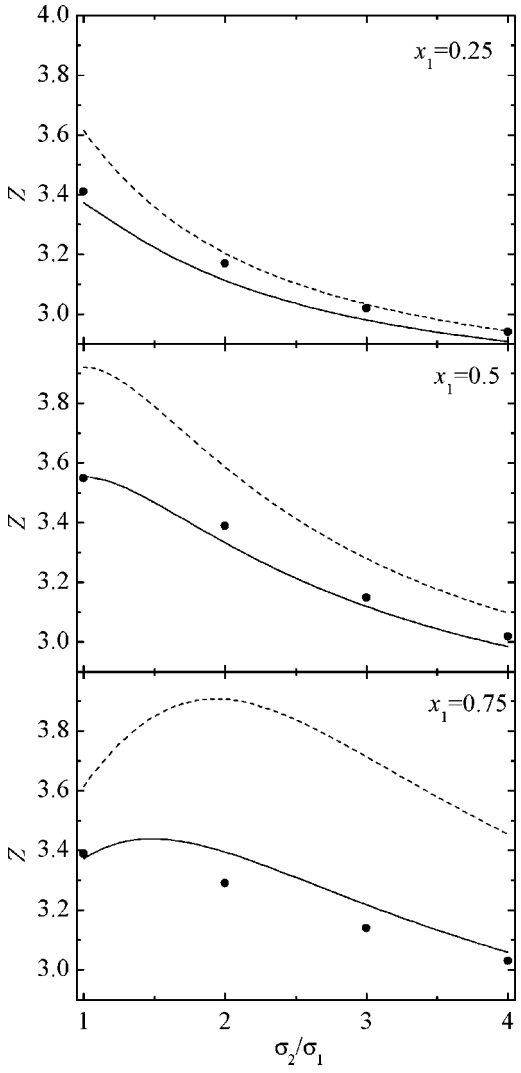

FIG. 9. Plot of the compressibility factor vs the size ratio σ_2/σ_1 for three binary mixtures of nonadditive hard disks with $\Delta=0.2$ at $\eta=0.4$ and $x_1=0.25$ (upper panel), $x_1=0.5$ (middle panel), and $x_1=0.75$ (lower panel). The solid lines are our proposal, Eq. (35), and the dashed lines are Hamad's proposal, Eq. (28). The circles are results from molecular dynamics simulations (Ref. 64).

first order in the density. Operationally, our proposed EOS for the nonadditive mixture [cf. Eq. (35)] is given explicitly in terms of the pure component EOS, and the second and third virial coefficients of the mixture. The former feature is shared with other proposals in the literature.[63,74,76,78] In any case, we find that the present EOS does a good job also in the nonadditive situation and represents a reasonable compromise between simplicity and accuracy. In comparison with Hamad's approach, which is also simple and reasonably accurate and which we have generalized here to arbitrary dimensionality, it has the advantage of being able to deal with asymmetric mixtures where the former faces greater difficulties.

Because the full assessment of our proposal involves so many facets, there are of course many issues that we have not addressed. We have only attempted to illustrate some of the consequences of employing our approximate EOS. The results in the preceding section illustrate a trend that we have observed with other values of the parameters, namely, that in general Hamad's proposal does a better job for negative nonadditivities (especially as the density is increased) while ours should be preferred in the case of positive nonadditivities, at least for $d=1$, $d=2$, and $d=3$. Nevertheless, one can see that the performance of our EOS is reasonably good in highly asymmetric mixtures, even for negative Δ. So in some sense, rather than strictly competing, our approach and Hamad's are complementary. It is also worth noting that here we have chosen to take our original recipe of the additive

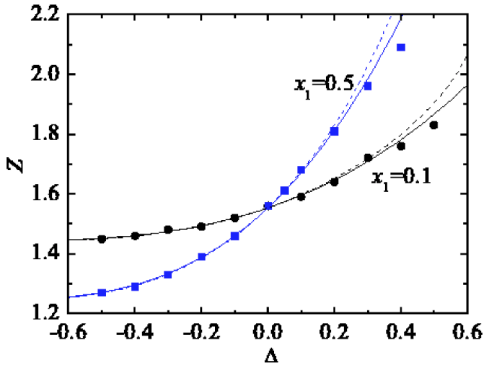

FIG. 10. Plot of the compressibility factor vs the nonadditivity parameter Δ for a symmetric binary mixture of nonadditive hard spheres at $\eta=\pi/30$ and two different compositions. The solid lines are our proposal, Eq. (35), and the dashed lines are Hamad's proposal, Eq. (28). The symbols are results from Monte Carlo simulations (Refs. 59 and 60).

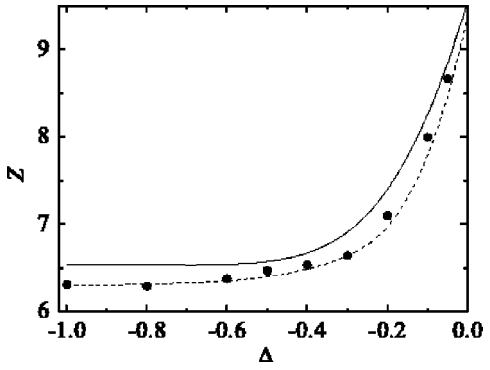

FIG. 11. Plot of the compressibility factor vs the nonadditivity parameter Δ for an equimolar asymmetric binary mixture of nonadditive hard spheres with size ratio $\sigma_2/\sigma_1=3$ at $\eta=0.5$. The solid line is our proposal, Eq. (35), and the dashed line is Hamad's proposal, Eq. (28). The circles are results from Monte Carlo simulations (Ref. 63).

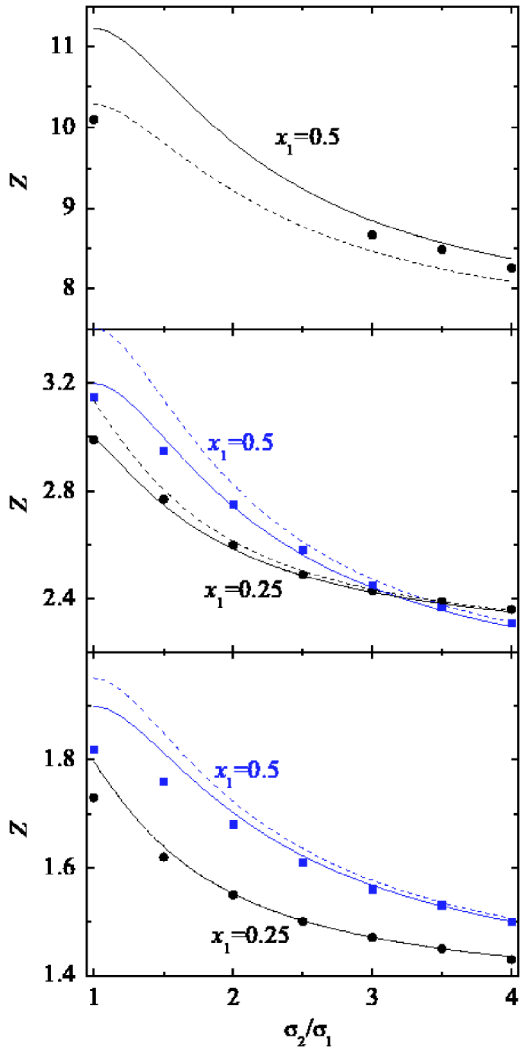

FIG. 12. Plot of the compressibility factor vs the size ratio σ_2/σ_1 for binary mixtures of nonadditive hard spheres with $x_1=0.5$, $\Delta=-0.05$, $\eta=0.5$ (upper panel), $x_1=0.25,0.5$, $\Delta=0.2$, $\eta=0.2$ (middle panel), and $x_1=0.25,0.5$, $\Delta=0.5$, $\eta=0.075$ (lower panel). The solid lines are our proposal, Eq. (35), and the dashed lines are Hamad's proposal, Eq. (28). The symbols are results from Monte Carlo simulations (Ref. 63).

case[80] for simplicity, but we could have as well considered the more refined ones that we introduced later,[81] at the expense of more complicated final expressions. Also, the choice of Z_{pure} is free and the results of course depend on that choice. Nevertheless, provided Z_{pure} is reasonably accurate, the qualitative trends should not be altered by different choices and this is actually the case. For instance, in the analysis of nonadditive hard disks we took for Z_{pure} the one corresponding to Luding's EOS.[85] With minor numerical differences, very similar results are obtained if Henderson's equation[87] or our EOS,[84] which are both accurate, are used instead. Analogously, in the three-dimensional case the results are practically the same if the Carnahan-Starling EOS[88] is used instead of Eq. (52).

We are fully aware that interesting features such as the demixing transition in the case of positive nonadditivity (both for symmetric and asymmetric mixtures) remain to be dealt with. We expect to examine some of these in the future. In any event, irrespective of the illustrative calculations that we have presented in this paper, we have attempted to include a rather comprehensive account of previous work on the subject which will hopefully serve to provide some perspective and be useful to other researchers.

ACKNOWLEDGMENTS

We want to thank Professor Oliver Penrose for providing the derivation of Ref. 8 to us and for a fruitful exchange of emails. This work was supported by Junta de Extremadura (Consejería de Educación y Tecnología) and Fondo Social Europeo under Project No. TEM04/0009. M.L.H. also wants to acknowledge D.G.A.P.A.-U.N.A.M. for a sabbatical grant. A.S. and S.B.Y. acknowledge the financial support of Ministerio de Educación y Ciencia (Spain) through Grant No. FIS2004-01399 (partially financed by FEDER funds).

APPENDIX A: EXACT SOLUTION IN THE ONE-DIMENSIONAL BINARY MIXTURE CASE

In the one-dimensional case ($d=1$) with nearest-neighbor interactions [which implies that $2\sigma_{12}\geqslant\max(\sigma_1,\sigma_2)$], the thermodynamic and structural properties of the binary mixture are exactly known.[1,3,6–8] The EOS relating the density ρ to the pressure p (in units of k_BT) and to the diameters σ_1, σ_2, and $\sigma_{12}=\frac{1}{2}(\sigma_1+\sigma_2)(1+\Delta)$ is given by

$$\frac{1}{\rho}=\frac{1}{p}+\alpha\frac{\sqrt{1+4x_1x_2(e^{2\alpha p}-1)}-1}{e^{2\alpha p}-1}+\langle\sigma\rangle, \tag{A1}$$

where $\alpha\equiv\sigma_{12}-(\sigma_1+\sigma_2)/2=(\sigma_1+\sigma_2)\Delta/2\geqslant-\min(\sigma_1/2,\sigma_2/2)$. Note that if $p\to\infty$ then $\eta\to1$ for $\alpha>0$, while $\eta\to[1-2(|\alpha|/\langle\sigma\rangle)\min(x_1,x_2)]^{-1}$ for $\alpha<0$.

Equation (A1) can alternatively be written as

$$p=\frac{\rho}{1-\eta}\Phi\left(x_1,\frac{\rho\alpha}{1-\eta}\right), \tag{A2}$$

where $\Phi(x_1,w)$ is the solution to

$$\Phi^{-1}=1+w\frac{1-\sqrt{1+4x_1x_2(e^{2w\Phi}-1)}}{e^{2w\Phi}-1} \tag{A3}$$

or, equivalently,

$$e^{2w\Phi}-1=2w\frac{2x_1x_2w-(1-\Phi^{-1})}{(1-\Phi^{-1})^2}. \tag{A4}$$

In principle, the compressibility factor is a function of four parameters: the number density ρ, the mole fraction x_1, the size ratio σ_2/σ_1, and the nonadditivity parameter α. However, the scaling relation (A2) shows that there are only two independent parameters: the mole fraction x_1 and the scaled parameter $w\equiv\rho\alpha/(1-\eta)$. More specifically [cf. Eq. (A2)],

$$Z(\rho)=\frac{1}{1-\eta}\Phi\left(x_1,\frac{\rho\alpha}{1-\eta}\right). \tag{A5}$$

Thus, $\Phi(x_1,w)$ measures the compressibility factor of the nonadditive mixture, relative to that of an additive mixture with the same packing fraction.

The expansion of the scaling function $\Phi(x_1,w)$ in powers of w is

$$\Phi(x_1,w)=\sum_{n=0}^{\infty}\Phi_n(x_1)w^n, \tag{A6}$$

where the first few terms are

$$\Phi_0=1,\quad \Phi_1=2x_1x_2,$$
$$\Phi_2=0,\quad \Phi_3=-4x_1^2x_2^2, \tag{A7}$$
$$\Phi_4=-\tfrac{8}{3}x_1^2x_2^2,\quad \Phi_5=-\tfrac{4}{3}x_1^2x_2^2(1-8x_1x_2).$$

In the limit of very small nonadditivity, we can make the linear approximation $\Phi(x_1,w)\approx 1+2x_1x_2w$. This is a good approximation in the range $-0.4\leqslant w\leqslant 0.4$. The asymptotic behaviors of $\Phi(x_1,w)$ are easily derived from Eqs. (A3) and (A4). In the limit $w\to\infty$ (with $\alpha>0$), we simply have $\Phi(x_1,w)\to 1$, while in the limit $w\to-\infty$, the result is $\Phi(x_1,w)\to -K(x_1)w^{-1}$, where $K(x_1)$ is the solution to

$$4x_1x_2K=1+\sqrt{1-4x_1x_2(1-e^{-2K})}. \tag{A8}$$

Note also that $\Phi(x_1,w)$ is a nonmonotonic function of w which presents a maximum for a certain value $w_0(x_1)>0$.

From Eqs. (A5)–(A7) it follows that the (exact) second and third virial coefficients can be written as

$$\overline{B}_2=\langle\sigma\rangle+2x_1x_2\alpha,\quad \overline{B}_3=\langle\sigma\rangle(\langle\sigma\rangle+4x_1x_2\alpha). \tag{A9}$$

Further, the fugacity $z_1\equiv e^{\mu_1}$ (where μ_1 is the chemical potential of species 1, again in units of k_BT) is given by the following expression:

$$z_1=\lambda_1 p e^{\sigma_1 p}\left(1-\frac{\Phi-1}{2x_1w\Phi}\right), \tag{A10}$$

and a similar expression for z_2.

1. Absence of phase separation

Given the values of σ_1, σ_2, and σ_{12} (or α), the thermodynamic state of the mixture is characterized by the pair (ρ_1,ρ_2) or, equivalently, by $[x_1,w\equiv\rho\alpha/(1-\eta)]$. Here we will adopt the latter viewpoint. If there would exist phase separation into two distinct phases A and B, the pressure and the chemical potentials should be equal in both phases. The pressure condition is equivalent to

$$w^{\mathrm{A}}\Phi(x_1^{\mathrm{A}},w^{\mathrm{A}})=w^{\mathrm{B}}\Phi(x_1^{\mathrm{B}},w^{\mathrm{B}}). \tag{A11}$$

The conditions on the chemical potentials yield

$$\frac{x_1^{\mathrm{A}}}{\Phi(x_1^{\mathrm{A}},w^{\mathrm{A}})-1}=\frac{x_1^{\mathrm{B}}}{\Phi(x_1^{\mathrm{B}},w^{\mathrm{B}})-1}, \tag{A12}$$

$$\frac{1-x_1^{\mathrm{A}}}{\Phi(x_1^{\mathrm{A}},w^{\mathrm{A}})-1}=\frac{1-x_1^{\mathrm{B}}}{\Phi(x_1^{\mathrm{B}},w^{\mathrm{B}})-1}. \tag{A13}$$

These two equations imply

$$x_1^{\mathrm{A}}=x_1^{\mathrm{B}}, \tag{A14}$$

$$\Phi(x_1^{\mathrm{A}},w^{\mathrm{A}})=\Phi(x_1^{\mathrm{A}},w^{\mathrm{B}}). \tag{A15}$$

Given the nonmonotonic behavior of Φ as a function of w, Eq. (A15) has solutions with $w^{\mathrm{A}}\neq w^{\mathrm{B}}$. However, the combination of Eqs. (A11) and (A15) means that

$$w^{\mathrm{A}}=w^{\mathrm{B}}, \tag{A16}$$

and so the only solution is the trivial one.

2. Distribution functions at contact

From Lebowitz and Zomick's paper[6] (and after some algebra), one can get the contact values

$$g_{11}=\frac{1}{1-\eta}\frac{2x_1w\Phi-(\Phi-1)}{2x_1^2w}, \tag{A17}$$

$$g_{22}=\frac{1}{1-\eta}\frac{2x_2w\Phi-(\Phi-1)}{2x_2^2w}, \tag{A18}$$

$$g_{12}=\sqrt{g_{11}g_{22}}e^{-w\Phi}. \tag{A19}$$

Using the expansion (A6), one has

$$g_{11}=\frac{1}{1-\eta}[1+2x_2w+2x_2^2w^2+O(w^3)], \tag{A20}$$

$$g_{22}=\frac{1}{1-\eta}[1+2x_1w+2x_1^2w^2+O(w^3)], \tag{A21}$$

$$g_{12}=\frac{1}{1-\eta}[1-2x_1x_2w^2+O(w^3)]. \tag{A22}$$

APPENDIX B: SOME SPECIAL LIMITS

It is interesting to examine the performance of Hamad's approximation, Eqs. (27) and (28), and of our proposal, Eqs. (31) and (35), in the following special limits.

1. $\sigma_{12}=0$

In the limit of extreme negative nonadditivity ($\sigma_{12}=0$ or $\Delta=-1$), one has $\hat{\sigma}_1=\hat{\sigma}_2=0$, so that Eq. (13) yields

$$c_{1;11}=\frac{b_3}{b_2}\sigma_1^d, \quad c_{2;22}=\frac{b_3}{b_2}\sigma_2^d,$$
$$c_{1;12}=c_{1;22}=c_{2;11}=c_{2;12}=0. \tag{B1}$$

The above expressions are exact in that limit. Hamad's proposal (27) becomes then

$$X_{11}=\frac{x_1\sigma_1^d}{\langle\sigma^d\rangle}, \quad X_{22}=\frac{x_2\sigma_2^d}{\langle\sigma^d\rangle}, \quad X_{12}=0, \tag{B2}$$

$$g_{11}^{\mathrm{H}}(\rho)=g_{\mathrm{pure}}(\eta_1), \quad g_{22}^{\mathrm{H}}(\rho)=g_{\mathrm{pure}}(\eta_2), \quad g_{12}^{\mathrm{H}}(\rho)=1, \tag{B3}$$

where $\eta_i=v_d\rho x_i\sigma_i^d$ is the partial packing fraction of species i. Equation (B3) is the exact result, reflecting the fact that in the limit $\sigma_{12}=0$ the mixture is actually made of two mutually independent one-component fluids. On the other hand, in our proposal we have

$$z_{11}=\frac{b_3x_1\sigma_1^d-b_2\langle\sigma^d\rangle}{(b_3-b_2)\langle\sigma^d\rangle}, \quad z_{12}=-\frac{b_2}{b_3-b_2}, \tag{B4}$$

$$g_{11}^{\mathrm{SYH}}(\rho)=\frac{1}{1-\eta}\frac{b_3x_2\sigma_2^d}{(b_3-b_2)\langle\sigma^d\rangle}+g_{\mathrm{pure}}(\eta)\frac{b_3x_1\sigma_1^d-b_2\langle\sigma^d\rangle}{(b_3-b_2)\langle\sigma^d\rangle}, \tag{B5}$$

$$g_{12}^{\mathrm{SYH}}(\rho)=\frac{1}{1-\eta}\frac{b_3}{b_3-b_2}-g_{\mathrm{pure}}(\eta)\frac{b_2}{b_3-b_2}, \tag{B6}$$

plus the equivalent expressions obtained by the exchange $1\leftrightarrow2$. Equations (B5) and (B6) are only exact to first order in the density.

2. Widom-Rowlinson limit

The WR limit ($\sigma_1=\sigma_2\to0$) represents an extreme case of positive nonadditivity ($\Delta\to\infty$). The coefficients $c_{k;ij}$ are

$$c_{1;11}=c_{1;12}=c_{2;12}=c_{2;22}=0, \quad c_{1;22}=c_{2;11}=(2\sigma_{12})^d. \tag{B7}$$

In this WR limit the packing fraction vanishes, so that the relevant density parameter is $\eta'=v_d\rho\sigma_{12}^d$. In Hamad's approximation,

$$\langle\sigma^d\rangle X_{11}=\frac{b_2^2}{2b_3}x_2\sigma_{12}^d, \quad \langle\sigma^d\rangle X_{12}=0, \tag{B8}$$

$$g_{11}^{\mathrm{H}}(\rho)=g_{\mathrm{pure}}\left(\frac{b_2^2}{2b_3}x_2\eta'\right), \quad g_{12}^{\mathrm{H}}(\rho)=1. \tag{B9}$$

Our approximation yields

$$\langle\sigma^d\rangle z_{11}=\frac{b_2^2x_2\sigma_{12}^d}{2(b_3-b_2)}, \quad \langle\sigma^d\rangle z_{12}=0, \tag{B10}$$

$$g_{11}^{\mathrm{SYH}}(\rho)=1+\frac{b_2}{2}x_2\eta', \quad g_{12}^{\mathrm{SYH}}(\rho)=1. \tag{B11}$$

Both approximations differ in $g_{11}(\rho)$ and $g_{22}(\rho)$, but these contact values do not contribute to $Z(\rho)$ in the WR limit. The result is in the two cases

$$Z(\rho)=1+2^dx_1x_2\eta', \tag{B12}$$

which is the mean-field result.

We note that in the one-dimensional case the exact result that follows when setting $\sigma_1=\sigma_2=0$, $\eta'=\rho\alpha$ in Eq. (A5) is

$$Z(\rho)=\Phi(x_1,\eta') \quad (d=1). \tag{B13}$$

3. Asakura-Oosawa limit

The Asakura-Oosawa limit consists of setting $\sigma_2=0$ and $\sigma_{12}=\sigma_1/2+R$, where R represents the radius of gyration. In that case, $\hat{\sigma}_1=\sigma_1+2R$ and $\hat{\sigma}_2=2R$, so that Eq. (13) gives

$$c_{1;11}=\frac{b_3}{b_2}\sigma_1^d, \quad c_{2;11}=(2R)^d+\left(\frac{b_3}{b_2}-1\right)\sigma_1(2R)^{d-1},$$
$$c_{1;22}=(\sigma_1+2R)^d, \quad c_{2;22}=0, \tag{B14}$$
$$c_{1;12}=\sigma_1^d+\left(\frac{b_3}{b_2}-1\right)\frac{4R\sigma_1^d}{\sigma_1+2R}, \quad c_{2;12}=0.$$

From Eq. (B14), it follows that

$$z_{11}=1+\frac{x_2}{x_1}\frac{b_2}{b_3-b_2}\left(\frac{2R}{\sigma_1}\right)^{d-1}\left(\frac{2R}{\sigma_1}+\frac{b_3}{b_2}-1\right), \tag{B15}$$

$$z_{22}=\frac{b_2}{b_3-b_2}\left[\left(1+\frac{2R}{\sigma_1}\right)^d-1\right], \tag{B16}$$

$$z_{12}=\frac{4R/\sigma_1}{1+2R/\sigma_1}. \tag{B17}$$

Further, in this limit $\langle\sigma^d\rangle=x_1\sigma_1^d$, $\overline{B}_2=2^{d-1}x_1[x_1\sigma_1^d+2(1-x_1)(\sigma_1/2+R)^d]$ and $\overline{B}_3$ may be computed from the $c_{k;ij}$ given in Eq. (B14). Therefore, upon substitution into Eq. (35), one would get the EOS for the Asakura-Oosawa limit. Since the resulting expression is not very illuminating, it will be omitted. Similarly, with the substitution of Eqs. (B15)–(B17) into Eq. (31) the contact values of the radial distribution functions (which will be also omitted) follow. The corresponding results for this limit in Hamad's proposal are readily derived from Eqs. (34) and (B15)–(B17), and subsequent substitution into Eqs. (27) and (28).

In $d=1$, taking the Asakura-Oosawa limit ($\sigma_2=0,\alpha=R$) in Eq. (A5) we have the exact result

$$Z(\rho)=\frac{1}{1-\eta}\Phi\left(x_1,\frac{\rho R}{1-\eta}\right) \quad (d=1). \tag{B18}$$

[1] I. Prigogine and S. Lafleur, Bull. Cl. Sci., Acad. R. Belg. **40**, 484 (1954); **40**, 497 (1954).
[2] S. Asakura and F. Oosawa, J. Chem. Phys. **22**, 1255 (1954); J. Polym. Sci. **33**, 183 (1958).
[3] R. Kikuchi, J. Chem. Phys. **23**, 2327 (1955).
[4] P. Ballone, G. Pastore, G. Galli, and D. Gazzillo, Mol. Phys. **59**, 275 (1986).
[5] D. Gazzillo, G. Pastore, and S. Enzo, J. Phys.: Condens. Matter **1**, 3469 (1989); D. Gazzillo, G. Pastore, and R. Frattini, *ibid.* **2**, 3469 (1990).
[6] J. Lebowitz and D. Zomick, J. Chem. Phys. **54**, 3335 (1971).
[7] D. S. Corti and R. K. Bowles, Mol. Phys. **96**, 1623 (1999).
[8] O. Penrose, http://www.ma.hw.ac.uk/~oliver/hardrods/notes.tex.

[9] H.-O. Carmesin, H. L. Frisch, and J. K. Percus, J. Stat. Phys. **63**, 791 (1991).
[10] B. Widom and J. S. Rowlinson, J. Chem. Phys. **52**, 1670 (1970).
[11] A. Vrij, Pure Appl. Chem. **48**, 471 (1976); A. P. Gast, C. K. Hall, and W. B. Russel, J. Colloid Interface Sci. **96**, 251 (1983); E. Canessa, M. J. Grimson, and M. Silbert, Mol. Phys. **67**, 1153 (1989); E. J. Meijer and D. Frenkel, Phys. Rev. Lett. **67**, 1110 (1991); H. N. W. Lekerkerker, W. C.-K. Poon, P. N. Pusey, A. Stroobants, and P. B. Warren, Europhys. Lett. **20**, 559 (1992); E. J. Meijer and D. Frenkel, J. Chem. Phys. **100**, 6873 (1994); A. Vrij, Physica A **235**, 120 (1997); T. Biben and J. P. Hansen, *ibid.* **235**, 142 (1997); M. Dijkstra, Phys. Rev. E **58**, 7523 (1998); M. Dijkstra, J. M. Brader, and R. Evans, J. Phys.: Condens. Matter **11**, 10079 (1999); A. A. Louis, R. Finken, and J.-P. Hansen, Europhys. Lett. **46**, 741 (1999); Phys. Rev. E **61**, R1028 (2000); R. Roth and R. Evans, Europhys. Lett. **53**, 271 (2001); D. Goulding and J.-P. Hansen, Mol. Phys. **99**, 865 (2001); A. A. Louis and R. Roth, J. Phys.: Condens. Matter **13**, L777 (2001); R. Roth, R. Evans, and A. A. Louis, Phys. Rev. E **64**, 051202 (2001); M. Schmidt and A. R. Denton, *ibid.* **65**, 061410 (2002); T. Bickel, J. Chem. Phys. **118**, 8960 (2003); R. L. C. Vink and J. Horbach, J. Phys.: Condens. Matter **16**, S3807 (2004); R. L. C. Vink, J. Horbach, and K. Binder, arXiv: cond-mat/0409099, 2004 (unpublished).
[12] D. Ruelle, Phys. Rev. Lett. **28**, 1019 (1972).
[13] H. L. Frisch and C. Carlier, Phys. Rev. Lett. **27**, 1040 (1971).
[14] T. W. Melnyck, J. L. Rowlinson, and B. L. Sawford, Mol. Phys. **24**, 809 (1972).
[15] J. P. Straley, M. A. Cotter, T.-J Lie, and B. Widom, J. Chem. Phys. **57**, 4484 (1972).
[16] B. Widom and F. H. Stillinger, J. Chem. Phys. **58**, 616 (1973).
[17] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959); E. Helfand, H. L. Frisch, and J. L. Lebowitz, *ibid.* **34**, 1037 (1961); J. L. Lebowitz, E. Helfand, and E. Praestgaard, *ibid.* **43**, 774 (1965).
[18] M. I. Guerrero, J. L. Rowlinson, and B. L. Sawford, Mol. Phys. **28**, 1603 (1974).
[19] S. Ahn and J. L. Lebowitz, J. Chem. Phys. **60**, 523 (1974).
[20] E. Bergmann, Mol. Phys. **32**, 237 (1976).
[21] R. Tenne and E. Bergmann, J. Chem. Phys. **70**, 1952 (1979).
[22] J. Karkheck and G. Stell, J. Chem. Phys. **71**, 3620 (1979).
[23] P. Borgelt, C. Hoheisel, and G. Stell, J. Chem. Phys. **92**, 6161 (1990).
[24] H. Luo, C. Hoheisel, and J. Karkheck, Phys. Rev. A **42**, 4609 (1990).
[25] G. Johnson, H. Gould, J. Machta, and L. K. Chayes, Phys. Rev. Lett. **79**, 2612 (1997).
[26] C.-Y. Shew and A. Yethiraj, J. Chem. Phys. **104**, 7665 (1996); K. Jagannathan and A. Yethiraj, *ibid.* **118**, 7907 (2003).
[27] A. Yethiraj and G. Stell, J. Stat. Phys. **100**, 39 (2000).
[28] R. Fantoni and G. Pastore, Physica A **332**, 349 (2004).
[29] K. Jagannathan and A. Yethiraj, Phys. Rev. Lett. **93**, 015701 (2004).
[30] E. Bergmann, Chem. Phys. Lett. **38**, 385 (1976).
[31] R. Tenne and E. Bergmann, Phys. Rev. A **17**, 2036 (1978).
[32] E. Bergmann and R. Tenne, Chem. Phys. Lett. **56**, 310 (1978).
[33] R. J. Bearman and R. M. Mazo, J. Chem. Phys. **88**, 1235 (1988); **91**, 1227 (1989).
[34] R. M. Mazo and R. J. Bearman, J. Chem. Phys. **93**, 6694 (1990).
[35] H. M. Schaink, Z. Naturforsch., A: Phys. Sci. **48**, 899 (1993).
[36] V. Ehrenberg, H. M. Schaink, and C. Hoheisel, Physica A **169**, 365 (1990).
[37] O. Penrose and J. L. Lebowitz, J. Math. Phys. **13**, 604 (1972).
[38] B. N. Perry and M. Silbert, Mol. Phys. **37**, 1823 (1979).
[39] J. H. Nixon and M. Silbert, Mol. Phys. **52**, 207 (1984).
[40] D. Gazzillo, J. Chem. Phys. **87**, 1757 (1987); Mol. Phys. **64**, 535 (1988); D. Gazzillo and G. Pastore, Chem. Phys. Lett. **159**, 388 (1989).
[41] D. Gazzillo, J. Chem. Phys. **95**, 4565 (1991).
[42] D. Gazzillo, Mol. Phys. **84**, 303 (1995).
[43] G. A. Martynov and G. N. Sarkisov, Mol. Phys. **49**, 1495 (1983).
[44] H. M. Schaink, Physica A **210**, 113 (1994).
[45] J. A. Anta and G. Kahl, Mol. Phys. **84**, 1273 (1995).
[46] E. Lomba, M. Alvarez, L. L. Lee, and N. G. Almarza, J. Chem. Phys. **104**, 4180 (1996).
[47] G. Kahl, B. Bildstein, and Y. Rosenfeld, Phys. Rev. E **54**, 5391 (1996).
[48] O. Sierra and Y. Duda, Phys. Lett. A **280**, 146 (2001).
[49] Y. Duda, E. Vakarin, and J. Alejandre, J. Colloid Interface Sci. **258**, 10 (2003).
[50] G. Pellicane, C. Caccamo, D. S. Wilson, and L. L. Lee, Phys. Rev. E **69**, 061202 (2004).
[51] T. W. Melnyck and B. L. Sawford, Mol. Phys. **29**, 891 (1975).
[52] H. M. Schaink and C. Hoheisel, J. Chem. Phys. **97**, 8561 (1992).
[53] D. J. Adams and I. R. McDonald, J. Chem. Phys. **63**, 1900 (1975).
[54] E. Dickinson, Mol. Phys. **33**, 1463 (1977).
[55] J. G. Amar, Mol. Phys. **67**, 739 (1989).
[56] C. Hoheisel, Phys. Rev. A **41**, 2076 (1990).
[57] R. D. Mountain and A. H. Harvey, J. Chem. Phys. **94**, 2238 (1991).
[58] M. Rovere and G. Pastore, J. Phys.: Condens. Matter **6**, A163 (1994).
[59] J. Jung, M. S. Jhon, and F. H. Ree, J. Chem. Phys. **100**, 528 (1994).
[60] J. Jung, M. S. Jhon, and F. H. Ree, J. Chem. Phys. **100**, 9064 (1994).
[61] J. Jung, M. S. Jhon, and F. H. Ree, J. Chem. Phys. **102**, 1349 (1995).
[62] Y. Rosenfeld, M. Schmidt, H. Löwen, and P. Tarazona, Phys. Rev. E **55**, 4245 (1997).
[63] E. Z. Hamad, Mol. Phys. **91**, 371 (1997).
[64] M. Al-Naafa, J. B. El-Yakubu, and E. Z. Hamad, Fluid Phase Equilib. **154**, 33 (1999).
[65] F. Saija, G. Pastore, and P. V. Giaquinta, J. Phys. Chem. B **102**, 10368 (1998).
[66] F. Saija and P. V. Giaquinta, J. Chem. Phys. **117**, 5780 (2002).
[67] W. T. Góźdź, J. Chem. Phys. **119**, 3309 (2003).
[68] R. Castañeda-Priego, A. Rodríguez-López, and J. M. Méndez-Alcaraz, J. Phys.: Condens. Matter **15**, S3393 (2003).
[69] M. Schmidt, J. Phys.: Condens. Matter **16**, L351 (2004).
[70] R. Fantoni and G. Pastore, J. Chem. Phys. **120**, 10681 (2004).
[71] A. Buhot, J. Chem. Phys. (in press).
[72] B. Barboy and W. M. Gelbart, J. Chem. Phys. **71**, 3053 (1979); J. Stat. Phys. **22**, 709 (1980).
[73] T. Kihara, Rev. Mod. Phys. **27**, 412 (1955).
[74] E. Z. Hamad, J. Chem. Phys. **105**, 3229 (1996).
[75] E. Z. Hamad, J. Chem. Phys. **101**, 10195 (1994).
[76] E. Z. Hamad, J. Chem. Phys. **105**, 3222 (1996).
[77] H. Hammawa and E. Z. Hamad, J. Chem. Soc., Faraday Trans. **92**, 4943 (1996).
[78] E. Z. Hamad and G. O. Yahaya, Fluid Phase Equilib. **168**, 59 (2000).
[79] B. F. Abu-Sharkh, A. Sunaidi, and E. Z. Hamad, J. Chem. Phys. **120**, 5795 (2004). The idea of using a nonadditive hard-sphere mixture as the reference system for other mixtures within the perturbation theory of fluids is not new. It was already used in the work of Harvey and Prausnitz [A. H. Harvey and J. M. Prausnitz, Fluid Phase Equilib. **48**, 1197 (1989)] and in a paper by Kahl [G. Kahl, J. Chem. Phys. **93**, 5105 (1990)].
[80] A. Santos, S. B. Yuste, and M. López de Haro, Mol. Phys. **96**, 1 (1999).
[81] A. Santos, S. B. Yuste, and M. López de Haro, J. Chem. Phys. **117**, 5785 (2002).
[82] F. Saija, G. Fiumara, and P. V. Giaquinta, J. Chem. Phys. **108**, 9098 (1998).
[83] A. Yu. Vlasov and A. J. Masters, Fluid Phase Equilib. **212**, 183 (2003).
[84] A. Santos, M. López de Haro, and S. B. Yuste, J. Chem. Phys. **103**, 4622 (1995); M. López de Haro, A. Santos, and S. B. Yuste, Eur. J. Phys. **19**, 281 (1998).
[85] S. Luding, Phys. Rev. E **63**, 042201 (2001); S. Luding and A. Santos, J. Chem. Phys. **121**, 8458 (2004).
[86] J. Kolafa (unpublished). This equation of state first appeared as Eq. (4.46) in the review paper by T. Boublík and I. Nezbeda, Collect. Czech. Chem. Commun. **51**, 2301 (1986).
[87] D. Henderson, Mol. Phys. **30**, 971 (1975).
[88] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).