

# Virial coefficients, thermodynamic properties, and fluid-fluid transition of nonadditive hard-sphere mixtures

Andrés Santos,<sup>a)</sup> Mariano López de Haro,<sup>b)</sup> and Santos B. Yuste<sup>c)</sup>  
*Departamento de Física, Universidad de Extremadura, E-06071 Badajoz, Spain*

(Received 28 January 2010; accepted 23 April 2010; published online 25 May 2010)

Different theoretical approaches for the thermodynamic properties and the equation of state for multicomponent mixtures of nonadditive hard spheres in  $d$  dimensions are presented in a unified way. These include the theory by Hamad, our previous formulation, the original MIX1 theory, a recently proposed modified MIX1 theory, as well as a nonlinear extension of the MIX1 theory proposed in this paper. Explicit expressions for the compressibility factor, Helmholtz free energy, and second, third, and fourth virial coefficients are provided. A comparison is carried out with recent Monte Carlo data for the virial coefficients of asymmetric mixtures and with available simulation data for the compressibility factor, the critical consolute point, and the liquid-liquid coexistence curves. The merits and limitations of each theory are pointed out. © 2010 American Institute of Physics. [doi:10.1063/1.3429600]

## I. INTRODUCTION

Nonadditive hard spheres represent a versatile model to study various real physical systems. These include alloys, aqueous electrolyte solutions, molten salts, rare gas mixtures, and colloids. In these systems homocoordination and heterocoordination may be interpreted in terms of excluded volume effects due to nonadditivity of the repulsive (hard-core) part of the intermolecular potential and so, for instance, the occurrence of liquid-liquid demixing in real systems may be linked to a binary hard-sphere mixture with positive nonadditivity, while negative nonadditivity may be invoked to explain chemical short-range order in amorphous and liquid binary mixtures with preferred heterocoordination. On the theoretical side, prototype models of nonadditive hard-sphere mixtures, such as the Widom–Rowlinson model<sup>1</sup> or the Asakura–Oosawa model,<sup>2</sup> have been very useful to gain insight into interesting physical aspects, such as fluid-fluid phase transitions and the nature of depletion forces.

A few years ago, in a paper<sup>3</sup> where a rather thorough review of the theoretical and simulation works on nonadditive hard-sphere mixtures was provided, we introduced an equation of state of multicomponent nonadditive hard-sphere mixtures in  $d$  dimensions. Such an equation of state results from a natural extension of the one we had earlier proposed for additive hard spheres,<sup>4</sup> has an explicit (simple) density dependence, and by construction leads to the exact second and third virial coefficients. In the case of  $d=3$ , in the same paper we compared the predictions for the compressibility factor corresponding to our proposal with those of the proposal by Hamad,<sup>5–8</sup> which shares some characteristics with

ours, and available simulation results for various binary mixtures.<sup>9–13</sup> We also compared the predictions of the fourth and fifth virial coefficients arising from the above two theoretical proposals and the then available Monte Carlo results.<sup>14,15</sup> The restriction in the comparison only to Hamad's approach was justified then by the fact that Hamad had already proved that his proposal was superior to other theories, including the so-called MIX1 theory originally due to Melnick and Sawford.<sup>16</sup>

Recently, Pellicane *et al.*<sup>17</sup> reported new evaluations of the fourth virial coefficient of a binary nonadditive hard-sphere mixture covering a wide range of size ratios and values of the nonadditivity parameter. Also recently, Paricaud<sup>18</sup> proposed a new equation of state for nonadditive hard-sphere mixtures, which is based on and corrects one of the deficiencies of the MIX1 theory, namely, the fact that MIX1 does not lead to the correct second virial coefficient. These two recent papers serve as a motivation for the present contribution. On the one hand, we want to see to what extent the conclusions drawn from the analysis carried out in Ref. 3 are still valid in view of the new available data. On the other hand, we will also introduce a (new) nonlinear extension of the MIX1 theory. As an extra bonus, we will write all the theoretical expressions in a unified language which will hopefully make the comparison much easier.

The paper is organized as follows. In order to make it self-contained, in Sec. II we provide the necessary background for the later development. Section III provides the explicit expressions for the contact values of the radial distribution functions, compressibility factors, Helmholtz free energies, and second, third, and fourth virial coefficients as given by the original MIX1 theory, Paricaud's modified MIX1 theory, Hamad's theory, and our earlier proposal. A nonlinear extension of the MIX1 theory is also introduced here. In Sec. IV we compare the numerical values of the composition-independent virial coefficients, compressibility

<sup>a)</sup>Electronic mail: andres@unex.es. URL: <http://www.unex.es/eweb/fisteor/andres/>.

<sup>b)</sup>Electronic mail: malopez@servidor.unam.mx. URL: <http://xml.cie.unam.mx/xml/tc/ft/mlh/>. On sabbatical leave from Centro de Investigación en Energía, Universidad Nacional Autónoma de México (U.N.A.M.), Temixco, Morelos 62580, Mexico.

<sup>c)</sup>Electronic mail: santos@unex.es. URL: <http://www.unex.es/fisteor/santos/>.

factors, and liquid-liquid coexistence curves for a variety of cases with available Monte Carlo data. This paper is closed in Sec. V with some concluding remarks.

## II. GENERAL BACKGROUND

We consider an  $N$ -component mixture of nonadditive hard spheres in  $d$  dimensions. Let  $\sigma_{ij}$  denote the hard-core distance of the interaction between a sphere of species  $i$  and a sphere of species  $j$ . If the diameter of a sphere of species  $i$  is  $\sigma_i \equiv \sigma_{ii}$ , then  $\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j)(1 + \Delta_{ij})$ , where  $\Delta_{ij} \geq -1$  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  $Z \equiv p / \rho k_B T$  of the nonadditive mixture, where  $\rho$  is the total number density,  $p$  is the pressure,  $T$  is the temperature, and  $k_B$  is the Boltzmann constant, is given by

$$Z(\rho, \{x_k\}, \{\sigma_{k\ell}\}) = 1 + 2^{d-1} v_d \rho \sum_{i,j=1}^N x_i x_j \sigma_{ij}^d g_{ij}(\rho, \{x_k\}, \{\sigma_{k\ell}\}), \quad (2.1)$$

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

$$g_{ij}(\rho) = 1 + v_d \rho \sum_{k=1}^N x_k c_{kij} + (v_d \rho)^2 \sum_{k,\ell=1}^N x_k x_\ell c_{k\ell ij} + O(\rho^3), \quad (2.2)$$

where the coefficients  $c_{kij}, c_{k\ell ij}, \dots$  are independent of the mole fractions but, in general, depend in a nontrivial way on the set of diameters  $\{\sigma_{ij}\}$ . To our knowledge, only the coefficients linear in  $\rho$  (i.e.,  $c_{kij}$ ) are known analytically for  $d \leq 3$ . This formal series expansion in the number density, Eq. (2.2), when substituted into Eq. (2.1), yields the virial expansion of  $Z$ , which we write in the form

$$\begin{aligned} Z(\rho) &= 1 + \sum_{n=1}^{\infty} \rho^n B_{n+1} = 1 + \rho \sum_{i,j=1}^N x_i x_j B_{ij} \\ &+ \rho^2 \sum_{i,j,k=1}^N x_i x_j x_k B_{ijk} + \rho^3 \sum_{i,j,k,\ell=1}^N x_i x_j x_k x_\ell B_{ijkl} \\ &+ O(\rho^4). \end{aligned} \quad (2.3)$$

Here  $B_n$  is the usual  $n$ th virial coefficient of the multicomponent mixture, which is a polynomial of degree  $n$  in the mole fraction,  $B_{ij}, \dots$  being composition-independent coefficients. In terms of the coefficients  $c_{kij}$  and  $c_{k\ell ij}$ , the composition-independent second, third, and fourth virial coefficients are given by

$$B_{ij} = 2^{d-1} v_d \sigma_{ij}^d, \quad (2.4)$$

$$B_{ijk} = \frac{2^{d-1} v_d^2}{3} (\sigma_{ij}^d c_{kij} + \sigma_{ik}^d c_{jik} + \sigma_{jk}^d c_{ijk}), \quad (2.5)$$

$$\begin{aligned} B_{ijkl} &= \frac{2^{d-1} v_d^3}{6} (\sigma_{ij}^d c_{k\ell ij} + \sigma_{ik}^d c_{j\ell ik} + \sigma_{jk}^d c_{i\ell jk} + \sigma_{i\ell}^d c_{jk i\ell} \\ &+ \sigma_{j\ell}^d c_{ik j\ell} + \sigma_{k\ell}^d c_{ij k\ell}). \end{aligned} \quad (2.6)$$

Along the path we have taken, the different theories for mixtures of nonadditive hard spheres in  $d$  dimensions may be related to different proposals for  $g_{ij}(\rho)$ . In Sec. III we provide the explicit expressions for the approximate proposals that we will consider in this paper, including a new nonlinear extension of the MIX1 theory.

## III. SOME APPROXIMATE THEORETICAL DEVELOPMENTS

### A. MIX1 approximation

The original MIX1 approximation,<sup>16</sup> which we will indicate with a superscript M, is equivalent to

$$\sigma_{ij}^d g_{ij}^M(\rho) = \left( \frac{\sigma_i + \sigma_j}{2} \right)^d \left\{ g_{ij}^{\text{add}}(\rho) + Y_{ij}^M \frac{\partial}{\partial \rho} [\rho g_{ij}^{\text{add}}(\rho)] \right\}, \quad (3.1)$$

where  $g_{ij}^{\text{add}}(\rho)$  are the contact values of the *additive* mixture and

$$Y_{ij}^M \equiv d \Delta_{ij}. \quad (3.2)$$

Inserting Eq. (3.1) into Eq. (2.1) one gets

$$\begin{aligned} Z^M(\rho) &= Z^{\text{add}}(\rho) + b_2 v_d \rho \sum_{i,j} x_i x_j \left( \frac{\sigma_i + \sigma_j}{2} \right)^d Y_{ij}^M \frac{\partial}{\partial \rho} [\rho g_{ij}^{\text{add}}(\rho)], \end{aligned} \quad (3.3)$$

with  $Z^{\text{add}}(\rho)$  as the compressibility factor of the additive mixture with the same sets of mole fractions  $\{x_k\}$  and diameters  $\{\sigma_k\}$ . The Helmholtz free energy per particle in the MIX1 theory is then

$$\begin{aligned} \frac{a^M(\rho)}{k_B T} &= -1 + \sum_i x_i \ln(x_i \rho \lambda_i^d) + \frac{a_{\text{ex}}^{\text{add}}(\rho)}{k_B T} \\ &+ b_2 v_d \rho \sum_{i,j} x_i x_j \left( \frac{\sigma_i + \sigma_j}{2} \right)^d Y_{ij}^M g_{ij}^{\text{add}}(\rho), \end{aligned} \quad (3.4)$$

where  $\lambda_i$  is the de Broglie wavelength of particles of species  $i$ ,  $a_{\text{ex}}^{\text{add}}(\rho)$  is the excess Helmholtz free energy per particle of the additive mixture and, for convenience, we have identified  $2^{d-1}$  with the reduced second virial coefficient in the one-component  $d$ -dimensional hard-sphere fluid  $b_2$ . The second, third, and fourth virial coefficients of the mixture are in turn given by

$$B_{ij}^M = b_2 v_d \left( \frac{\sigma_i + \sigma_j}{2} \right)^d (1 + Y_{ij}^M), \quad (3.5)$$

$$B_{ijk}^M = \frac{b_2 v_d^2}{3} \left[ \left( \frac{\sigma_i + \sigma_j}{2} \right)^d c_{k;ij}^{\text{add}} (1 + 2Y_{ij}^M) + \left( \frac{\sigma_i + \sigma_k}{2} \right)^d \right. \\ \left. \times c_{j;ik}^{\text{add}} (1 + 2Y_{ik}^M) + \left( \frac{\sigma_j + \sigma_k}{2} \right)^d c_{i;jk}^{\text{add}} (1 + 2Y_{jk}^M) \right], \quad (3.6)$$

$$B_{ijkl}^M = \frac{b_2 v_d^3}{6} \left[ \left( \frac{\sigma_i + \sigma_j}{2} \right)^d c_{k\ell;ij}^{\text{add}} (1 + 3Y_{ij}^M) \right. \\ \left. + \left( \frac{\sigma_i + \sigma_k}{2} \right)^d c_{j\ell;ik}^{\text{add}} (1 + 3Y_{ik}^M) + \left( \frac{\sigma_i + \sigma_\ell}{2} \right)^d \right. \\ \left. \times c_{jk;i\ell}^{\text{add}} (1 + 3Y_{i\ell}^M) + \left( \frac{\sigma_j + \sigma_k}{2} \right)^d \right. \\ \left. \times c_{i\ell;jk}^{\text{add}} (1 + 3Y_{jk}^M) + \left( \frac{\sigma_j + \sigma_\ell}{2} \right)^d c_{ik;j\ell}^{\text{add}} (1 + 3Y_{j\ell}^M) \right. \\ \left. \times \left( \frac{\sigma_k + \sigma_\ell}{2} \right)^d c_{ij;k\ell}^{\text{add}} (1 + 3Y_{k\ell}^M) \right]. \quad (3.7)$$

In Eqs. (3.6) and (3.7),  $c_{k;ij}^{\text{add}}$  and  $c_{k\ell;ij}^{\text{add}}$  correspond to the coefficients in the expansion of  $g_{ij}^{\text{add}}(\rho)$  in powers of the number density. Note that the second virial coefficient of the mixture in the MIX1 theory is not exact [compare Eqs. (2.4) and (3.5)], except to first order in  $\Delta_{ij}$ . This problem can be traced back to the fact that according to Eq. (3.1),

$$\lim_{\rho \rightarrow 0} g_{ij}^M(\rho) = \frac{1 + Y_{ij}^M}{(1 + \Delta_{ij})^d} \neq 1. \quad (3.8)$$

This is remedied by Paricaud's modification<sup>18</sup> that is described in Sec. III B.

### B. Paricaud's modified MIX1 theory (mMIX1)

In the modification of the MIX1 theory introduced recently by Paricaud,<sup>18</sup> which we will refer to as mMIX1 and ascribe a superscript mM, one keeps Eq. (3.1), and hence Eqs. (3.3)–(3.7), except that  $Y_{ij}^M$  is replaced by

$$Y_{ij}^{\text{mM}} \equiv (1 + \Delta_{ij})^d - 1. \quad (3.9)$$

With this change  $Y_{ij}^M \rightarrow Y_{ij}^{\text{mM}}$ , Eq. (3.1) becomes

$$\sigma_{ij}^d g_{ij}^{\text{mM}}(\rho) = \left( \frac{\sigma_i + \sigma_j}{2} \right)^d \left\{ g_{ij}^{\text{add}}(\rho) - \frac{\partial}{\partial \rho} [\rho g_{ij}^{\text{add}}(\rho)] \right\} \\ + \sigma_{ij}^d \frac{\partial}{\partial \rho} [\rho g_{ij}^{\text{add}}(\rho)] \quad (3.10)$$

or equivalently,

$$g_{ij}^{\text{mM}}(\rho) = g_{ij}^{\text{add}}(\rho) + \frac{Y_{ij}^{\text{mM}}}{1 + Y_{ij}^{\text{mM}}} \rho \frac{\partial}{\partial \rho} g_{ij}^{\text{add}}(\rho). \quad (3.11)$$

In this way, instead of Eq. (3.8), we have  $\lim_{\rho \rightarrow 0} g_{ij}^{\text{mM}}(\rho) = 1$  and thus the second virial coefficient becomes exact. Otherwise, the third and higher virial coefficients are still approximate. In particular, the third and fourth virial coefficients are given by Eqs. (3.6) and (3.7), respectively, with  $Y_{ij}^M \rightarrow Y_{ij}^{\text{mM}}$ .

### C. Hamad's proposal

Hamad's approximation,<sup>5–8</sup> denoted by a superscript H, consists of proposing the following ansatz:

$$g_{ij}^H(\rho) = g^{\text{pure}}(y)|_{y=\eta X_{ij}^H}, \quad (3.12)$$

where  $g^{\text{pure}}(y)$  is the contact value of the radial distribution function of the one-component  $d$ -dimensional hard-sphere fluid at the packing fraction  $y$ ,  $\eta \equiv v_d \rho \langle \sigma^d \rangle$  is the packing fraction of the mixture (with  $\langle \sigma^m \rangle = \sum_{i=1}^N x_i \sigma_i^m$ ), and  $X_{ij}^H$  will be specified later. From Eq. (3.12) it follows that the virial expansion of  $g_{ij}(\rho)$  is given by

$$g_{ij}^H(\rho) = 1 + \sum_{n=1}^{\infty} \frac{b_{n+2}}{b_2} (v_d \rho \langle \sigma^d \rangle X_{ij}^H)^n, \quad (3.13)$$

where  $b_n$  is the reduced  $n$ th virial coefficient of the one-component  $d$ -dimensional hard-sphere fluid. In particular, comparing Eq. (3.13) with Eq. (2.2), one gets

$$\sum_k x_k c_{k;ij}^H = \frac{b_3}{b_2} \langle \sigma^d \rangle X_{ij}^H, \quad (3.14)$$

$$\sum_{k,\ell} x_k x_\ell c_{k\ell;ij}^H = \frac{b_4 b_2}{b_3^2} \left( \sum_k x_k c_{k;ij}^H \right)^2, \quad (3.15)$$

so that

$$c_{k\ell;ij}^H = \frac{b_4 b_2}{b_3^2} c_{k;ij}^H c_{\ell;ij}^H. \quad (3.16)$$

By requiring Eq. (3.12) to be exact to first order in density (third virial coefficient), i.e.,  $c_{k;ij}^H = c_{k;ij}$ , one must have

$$X_{ij}^H = \frac{b_2 \sum_k x_k c_{k;ij}}{b_3 \langle \sigma^d \rangle}. \quad (3.17)$$

Using the above results, the compressibility factor and Helmholtz free energy per particle in Hamad's proposal are given by

$$Z^H(\rho) = 1 + \sum_{ij} \frac{x_i x_j \sigma_{ij}^d Z^{\text{pure}}(\eta X_{ij}^H) - 1}{\langle \sigma^d \rangle X_{ij}^H} \quad (3.18)$$

and

$$\frac{a^H(\rho)}{k_B T} = -1 + \sum_i x_i \ln(x_i \rho \lambda_i^d) + \sum_{ij} \frac{x_i x_j \sigma_{ij}^d a_{\text{ex}}^{\text{pure}}(\eta X_{ij}^H)}{\langle \sigma^d \rangle X_{ij}^H k_B T}, \quad (3.19)$$

respectively, where  $Z^{\text{pure}}(y)$  and  $a_{\text{ex}}^{\text{pure}}(y)$  are the compressibility factor and the excess Helmholtz free energy per particle, respectively, of the one-component  $d$ -dimensional hard-sphere fluid at the packing fraction  $y$ . From Eqs. (2.6) and (3.16) it follows that the fourth virial coefficient in Hamad's approximation is

$$B_{ijkl}^H = \frac{b_4 b_2^2}{6 b_3^2} v_d^3 (\sigma_{ij}^d c_{k;ij} c_{\ell;ij} + \sigma_{ik}^d c_{j;ik} c_{\ell;ik} + \sigma_{i\ell}^d c_{j;i\ell} c_{k;i\ell} \\ + \sigma_{jk}^d c_{i;jk} c_{\ell;jk} + \sigma_{j\ell}^d c_{i;j\ell} c_{k;j\ell} + \sigma_{k\ell}^d c_{i;k\ell} c_{j;k\ell}). \quad (3.20)$$

In general, Eq. (3.18) yields

$$B_n^H = b_n v_d^{n-1} \left( \frac{b_2}{b_3} \right)^{n-2} \sum_{i,j} x_i x_j \sigma_{ij}^d \left( \sum_k x_k c_{k;ij} \right)^{n-2}. \quad (3.21)$$

#### D. The Santos–López de Haro–Yuste (SHY) proposal

In Ref. 3 we proposed the following ansatz (hereafter referred to as the SHY proposal) for the contact values of the radial distribution functions:

$$g_{ij}^{\text{SHY}}(\rho) = \frac{1}{1-\eta} + \left[ g^{\text{pure}}(\eta) - \frac{1}{1-\eta} \right] z_{ij}, \quad (3.22)$$

where

$$z_{ij} = \left( \frac{b_3}{b_2} - 1 \right)^{-1} \left( \frac{\sum_k x_k c_{k;ij}}{\langle \sigma^d \rangle} - 1 \right). \quad (3.23)$$

This choice guarantees that  $g_{ij}^{\text{SHY}}(\rho)$  is exact to first order in density and thus this approximation retains the exact second and third virial coefficients. When Eqs. (3.22) and (3.23) are inserted into Eq. (2.1) one gets

$$Z^{\text{SHY}}(\rho) = 1 + \frac{b_3 B_2^* - b_2 B_3^*}{b_3 - b_2} \frac{\eta}{1-\eta} + \frac{B_3^* - B_2^*}{b_3 - b_2} [Z^{\text{pure}}(\eta) - 1], \quad (3.24)$$

where we have called  $B_n^* \equiv B_n / (v_d \langle \sigma^d \rangle)^{n-1}$ ; note that  $B_n^* \rightarrow b_n$  in the one-component limit. In Eq. (3.24) we have expressed  $Z^{\text{SHY}}(\rho) - 1$  as a linear combination of  $\eta / (1-\eta)$  and  $Z^{\text{pure}}(\eta) - 1$ , with coefficients such that the second and third virial coefficients of the mixture are exactly reproduced. From approximation (3.24), one may easily derive the Helmholtz free energy per particle, which turns out to be

$$\begin{aligned} \frac{a^{\text{SHY}}(\rho)}{k_B T} = & -1 + \sum_i x_i \ln(x_i \rho \lambda_i^d) - \frac{b_3 B_2^* - b_2 B_3^*}{b_3 - b_2} \\ & \times \ln(1-\eta) + \frac{B_3^* - B_2^*}{b_3 - b_2} \frac{a_{\text{ex}}^{\text{pure}}(\eta)}{k_B T}. \end{aligned} \quad (3.25)$$

Also, Eq. (3.24) implies that the  $n$ th virial coefficient is given by

$$B_n^{\text{SHY}} = (v_d \langle \sigma^d \rangle)^{n-1} \left( \frac{b_n - b_2}{b_3 - b_2} B_3^* - \frac{b_n - b_3}{b_3 - b_2} B_2^* \right), \quad (3.26)$$

while for the composition-independent fourth virial coefficients one gets the following explicit expression:

$$\begin{aligned} B_{ijkl}^{\text{SHY}} = & \frac{v_d(b_4 - b_2)}{4(b_3 - b_2)} (\sigma_i^d B_{jkl} + \sigma_j^d B_{ikl} + \sigma_k^d B_{ijl} + \sigma_l^d B_{ijk}) \\ & - \frac{v_d^2(b_4 - b_3)}{6(b_3 - b_2)} (\sigma_i^d \sigma_j^d B_{kl} + \sigma_i^d \sigma_k^d B_{jl} + \sigma_i^d \sigma_l^d B_{jk} \\ & + \sigma_j^d \sigma_k^d B_{il} + \sigma_j^d \sigma_l^d B_{ik} + \sigma_k^d \sigma_l^d B_{ij}). \end{aligned} \quad (3.27)$$

#### E. A nonlinear MIX1 theory

As a final theoretical proposal, in this subsection we introduce a new extension of the MIX1 theory. The SHY approximation, Eq. (3.22), is a “local” approximation with respect to density in the sense that the nonadditive contact

value is expressed in terms of a reference contact value (here that of the one-component system) evaluated at precisely the *same* density. Analogously, both the original MIX1 approximation, Eq. (3.1), and Paricaud’s modified version, Eq. (3.11), can be termed “linearly nonlocal” since the nonadditive contact value is furthermore expressed in terms of the *first* density derivative of the additive contact value. In contrast, Hamad’s approximation, Eq. (3.12), is “nonlinearly nonlocal” because the reference contact value (again that of the one-component system) is taken at a totally *different* scaled density.

Our *nonlinear* MIX1 (nlMIX1) approximation, labeled with nlM, is inspired in both Eqs. (3.11) and (3.12). It consists of assuming that

$$g_{ij}^{\text{nlM}}(\rho) = g_{ij}^{\text{add}}(\rho X_{ij}^{\text{nlM}}), \quad (3.28)$$

where

$$X_{ij}^{\text{nlM}} \equiv 1 + \frac{Y_{ij}^{\text{mM}}}{1 + Y_{ij}^{\text{mM}}}. \quad (3.29)$$

Expanding in powers of  $X_{ij}^{\text{nlM}} - 1$ , Eq. (3.28) can be formally rewritten as

$$g_{ij}^{\text{nlM}}(\rho) = g_{ij}^{\text{add}}(\rho) + \sum_{n=1}^{\infty} \frac{1}{n!} \left( \frac{Y_{ij}^{\text{mM}}}{1 + Y_{ij}^{\text{mM}}} \rho \right)^n \frac{\partial^n}{\partial \rho^n} g_{ij}^{\text{add}}(\rho). \quad (3.30)$$

A comparison with Eq. (3.11) shows that  $g_{ij}^{\text{mM}}(\rho)$  can be seen as a first-order approximation of  $g_{ij}^{\text{nlM}}(\rho)$ . Using Eq. (3.28), the equation of state and Helmholtz free energy per particle corresponding to the nlMIX1 theory are given by

$$Z^{\text{nlM}}(\rho) = 1 + b_2 v_d \rho \sum_{i,j} x_i x_j \sigma_{ij}^d g_{ij}^{\text{add}}(\rho X_{ij}^{\text{nlM}}), \quad (3.31)$$

$$\begin{aligned} \frac{a^{\text{nlM}}(\rho)}{k_B T} = & -1 + \sum_i x_i \ln(x_i \rho \lambda_i^d) \\ & + b_2 \sum_{i,j} \frac{x_i x_j \sigma_{ij}^d}{\langle \sigma^d \rangle X_{ij}^{\text{nlM}}} \mathcal{G}_{ij}^{\text{add}}(\rho X_{ij}^{\text{nlM}}), \end{aligned} \quad (3.32)$$

respectively, where

$$\mathcal{G}_{ij}^{\text{add}}(\rho) \equiv v_d \langle \sigma^d \rangle \int_0^\rho d\rho' g_{ij}^{\text{add}}(\rho'). \quad (3.33)$$

Note that since  $g_{ij}^{\text{mM}}(\rho)$  and  $g_{ij}^{\text{nlM}}(\rho)$  coincide to first order in density, both give the same (approximate) third virial coefficient, namely, Eq. (3.6) with  $Y_{ij}^{\text{M}} \rightarrow Y_{ij}^{\text{mM}}$ . However, the mMIX1 and nlMIX1 theories differ at the level of the fourth virial coefficient. In this case, instead of Eq. (3.7) (with  $Y_{ij}^{\text{M}} \rightarrow Y_{ij}^{\text{mM}}$ ) we have



$$\begin{aligned}
B_{ijk\ell}^{\text{nlM}} = & \frac{b_2 v_d^3}{6} \left[ \left( \frac{\sigma_i + \sigma_j}{2} \right)^d c_{k\ell;ij}^{\text{add}} \frac{(1 + 2Y_{ij}^{\text{mM}})^2}{1 + Y_{ij}^{\text{mM}}} \right. \\
& + \left( \frac{\sigma_i + \sigma_k}{2} \right)^d c_{j\ell;ik}^{\text{add}} \frac{(1 + 2Y_{ik}^{\text{mM}})^2}{1 + Y_{ik}^{\text{mM}}} \\
& + \left( \frac{\sigma_i + \sigma_\ell}{2} \right)^d c_{jk;i\ell}^{\text{add}} \frac{(1 + 2Y_{i\ell}^{\text{mM}})^2}{1 + Y_{i\ell}^{\text{mM}}} \\
& + \left( \frac{\sigma_j + \sigma_k}{2} \right)^d c_{i\ell;jk}^{\text{add}} \frac{(1 + 2Y_{jk}^{\text{mM}})^2}{1 + Y_{jk}^{\text{mM}}} \\
& + \left( \frac{\sigma_j + \sigma_\ell}{2} \right)^d c_{ik;j\ell}^{\text{add}} \frac{(1 + 2Y_{j\ell}^{\text{mM}})^2}{1 + Y_{j\ell}^{\text{mM}}} \\
& \left. + \left( \frac{\sigma_k + \sigma_\ell}{2} \right)^d c_{ij;k\ell}^{\text{add}} \frac{(1 + 2Y_{k\ell}^{\text{mM}})^2}{1 + Y_{k\ell}^{\text{mM}}} \right]. \quad (3.34)
\end{aligned}$$

It would be tempting to determine  $X_{ij}^{\text{nlM}}$  in Eq. (3.28) by requiring agreement with the exact result to first order in density. This would give

$$X_{ij} \rightarrow \frac{\sum_k x_k c_{k;ij}}{\sum_k x_k c_{k;ij}^{\text{add}}}. \quad (3.35)$$

Unfortunately, however, this implies a wrong composition dependence of the higher order terms in the expansion of  $g_{ij}(\rho)$  in powers of  $\rho$ . In particular,

$$\sum_{k,\ell} x_k x_\ell c_{k\ell;ij} \rightarrow \left( \frac{\sum_k x_k c_{k;ij}}{\sum_k x_k c_{k;ij}^{\text{add}}} \right)^2 \sum_{k,\ell} x_k x_\ell c_{k\ell;ij}^{\text{add}}. \quad (3.36)$$

While the left-hand side is quadratic in the mole fractions, the right-hand side is the ratio between a quartic function and a quadratic function. In order to avoid inconsistencies as in Eq. (3.36) we need  $X_{ij}^{\text{nlM}}$  to be independent of the mole fractions. Apart from that,  $X_{ij}^{\text{nlM}}$  can be freely chosen but we will keep the choice (3.29) in order to make contact with the mMIX1 theory.

Before closing this section, it is worth noting that by construction, the nMIX1 theory is *a priori* not expected to be accurate for strong negative nonadditivities. This is because on physical grounds, the parameter  $X_{ij}^{\text{nlM}}$  defined by Eq. (3.29) must be positive definite. This in turn implies, from Eq. (3.9), the condition  $\Delta_{ij} > -(1 - 2^{-1/d})$ . In the three-dimensional case, the above condition becomes  $\Delta_{ij} \geq -0.21$ . As a matter of fact, expansion (3.30) does not converge if  $\Delta_{ij} \leq -(1 - 2^{-1/d})$ . Notwithstanding this, from a practical point of view the nMIX1 theory keeps providing meaningful results even if  $\Delta_{ij} \leq -(1 - 2^{-1/d})$ , as will be seen in Sec. IV.

## IV. RESULTS

Thus far the development has been rather general in the sense that all the approximations we have discussed apply for any number of components  $N$  in the mixture and any dimensionality  $d$ . However, it is only formal unless one specifies  $Z^{\text{add}}(\rho)$ ,  $a_{\text{ex}}^{\text{add}}(\rho)$ , and  $g_{ij}^{\text{add}}(\rho)$  in the case of all the MIX1 theories, and  $g^{\text{pure}}(y)$ ,  $Z^{\text{pure}}(y)$ ,  $a_{\text{ex}}^{\text{pure}}(y)$ , and  $c_{k;ij}$  in the cases of Hamad's and the SHY approximations. In Ref. 3 we introduced for general  $d$  the following approximation:

$$c_{k;ij} = \sigma_{k;ij}^d + \left( \frac{b_3}{b_2} - 1 \right) \frac{\sigma_{i;jk} \sigma_{j;ik}}{\sigma_{ij}} \sigma_{k;ij}^{d-1}, \quad (4.1)$$

where

$$\sigma_{k;ij} \equiv \sigma_{ik} + \sigma_{jk} - \sigma_{ij}. \quad (4.2)$$

This is exact when  $d=1$  and  $d=3$  and also proved to be accurate for  $d=2$ . We will also use it here.

As for the other remaining quantities, since the new numerical data<sup>17</sup> have been obtained for  $d=3$ , we will restrict ourselves in the subsequent analysis only to this dimensionality. Therefore in the MIX1 theories we will take for  $Z^{\text{add}}(\rho)$  and  $a_{\text{ex}}^{\text{add}}(\rho)$  the expressions given by the popular Boublik–Mansoori–Carnahan–Starling–Leland (BMCSL) equation of state,<sup>19,20</sup> namely,

$$Z^{\text{add}}(\rho) = \frac{1}{1-\eta} + \frac{3\eta}{(1-\eta)^2} \frac{\langle \sigma \rangle \langle \sigma^2 \rangle}{\langle \sigma^3 \rangle} + \frac{\eta^2 (3-\eta) \langle \sigma^2 \rangle^3}{(1-\eta)^3 \langle \sigma^3 \rangle^2}, \quad (4.3)$$

$$\begin{aligned}
\frac{a_{\text{ex}}^{\text{add}}(\rho)}{k_B T} = & -\ln(1-\eta) + \frac{3\eta}{1-\eta} \frac{\langle \sigma \rangle \langle \sigma^2 \rangle}{\langle \sigma^3 \rangle} \\
& + \left[ \frac{\eta}{(1-\eta)^2} + \ln(1-\eta) \right] \frac{\langle \sigma^2 \rangle^3}{\langle \sigma^3 \rangle^2}, \quad (4.4)
\end{aligned}$$

while for  $g_{ij}^{\text{add}}(\rho)$  the choice will be the Boublik–Grundke–Henderson–Lee–Levesque (BGHLL) values<sup>19,21,22</sup> given by

$$\begin{aligned}
g_{ij}^{\text{add}}(\rho) = & \frac{1}{1-\eta} + \frac{3\eta}{(1-\eta)^2} \frac{\sigma_i \sigma_j \langle \sigma^2 \rangle}{(\sigma_i + \sigma_j) \langle \sigma^3 \rangle} \\
& + \frac{2\eta^2}{(1-\eta)^3} \left[ \frac{\sigma_i \sigma_j \langle \sigma^2 \rangle}{(\sigma_i + \sigma_j) \langle \sigma^3 \rangle} \right]^2. \quad (4.5)
\end{aligned}$$

It follows from Eq. (4.5) that  $c_{k;ij}^{\text{add}}$  and  $c_{k\ell;ij}^{\text{add}}$  are given by

$$c_{k;ij}^{\text{add}} = \sigma_k^3 + 3 \frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j} \sigma_k^2, \quad (4.6)$$

$$c_{k\ell;ij}^{\text{add}} = \sigma_k^3 \sigma_\ell^3 \left[ 1 + 3 \frac{\sigma_i \sigma_j}{\sigma_i + \sigma_j} \frac{\sigma_k + \sigma_\ell}{\sigma_k \sigma_\ell} + 2 \frac{\sigma_i^2 \sigma_j^2}{\sigma_k \sigma_\ell (\sigma_i + \sigma_j)^2} \right]. \quad (4.7)$$

Equation (4.6) is exact and agrees with Eq. (4.1) in the three-dimensional additive limit ( $b_3/b_2 = \frac{5}{2}$ ,  $\sigma_{k;ij} \rightarrow \sigma_k$ ). On the other hand, Eq. (4.7) is approximate. According to Eq. (4.5), the quantity defined by Eq. (3.33) is given by

$$\begin{aligned}
\mathcal{G}_{ij}^{\text{add}}(\rho) = & -\ln(1-\eta) + 3 \left[ \frac{\eta}{1-\eta} + \ln(1-\eta) \right] \\
& \times \frac{\sigma_i \sigma_j \langle \sigma^2 \rangle}{(\sigma_i + \sigma_j) \langle \sigma^3 \rangle} - 2 \left[ \frac{(1-3\eta/2)\eta}{(1-\eta)^2} + \ln(1-\eta) \right] \\
& \times \left[ \frac{\sigma_i \sigma_j \langle \sigma^2 \rangle}{(\sigma_i + \sigma_j) \langle \sigma^3 \rangle} \right]^2. \quad (4.8)
\end{aligned}$$

Finally, in the case of the pure system, we will consider the expressions corresponding to the Carnahan–Starling (CS) equation of state,<sup>23</sup> namely,

$$g^{\text{pure}}(y) = \frac{1-y/2}{(1-y)^3}, \quad (4.9)$$

$$Z^{\text{pure}}(y) = \frac{1+y+y^2-y^3}{(1-y)^3}, \quad (4.10)$$

$$\frac{a_{\text{ex}}^{\text{pure}}(y)}{k_B T} = \frac{(4-3y)y}{(1-y)^2}. \quad (4.11)$$

With the above choices, all five approximations reduce to the CS equation of state in the one-component case  $\sigma_i = \sigma$ . In the additive limit, however, there are three independent proposals: BMCSL (to which the original MIX1 theories and its two variants, mMIX1 and nlMIX1, reduce), Hamad's, and what we referred to as eCS in Ref. 4. Of course, when non-additivity is introduced, the five approximations differ from each other.

### A. Virial coefficients

Figures 1–6 show the comparison of the values of the composition-independent fourth virial coefficients, as given by the five theoretical proposals considered in this paper, with the recent data of Pellicane *et al.*<sup>17,24</sup> One can immediately see that in the cases of  $B_{1112}$  and  $B_{1222}$  the best overall performance is the one of the nlMIX1 theory, followed closely by Hamad's approximation. Also worth noting is that the mMIX1 theory already does a very good job, especially for the smaller size ratios, while the original MIX1 theory gives the poorest agreement. As far as  $B_{112}$  is concerned, the agreement of the theoretical predictions with the Monte Carlo data is much less satisfactory, getting poorer as the nonadditivity parameter is increased. Here, no approximation is able to capture the negative values obtained by the Monte Carlo method for  $\Delta \geq 0.2$  and Hamad's approximation totally fails for small size ratios, irrespective of the value of the nonadditivity parameter. This is due to the fact that while the four remaining theories correctly reproduce the scaling behavior  $B_{1122} \sim \sigma_1^6 \sigma_2^3$  in the high-disparity limit  $\sigma_2/\sigma_1 \rightarrow 0$ , Hamad's proposal yields  $B_{1122} \sim \sigma_1^9$  in that limit. If one had to make a choice for this coefficient  $B_{1122}$ , either the SHY proposal or the original MIX1 theory would perhaps be the ones to go for (especially for  $0 \leq \Delta \leq 0.2$  and  $0.3 \leq \sigma_2/\sigma_1 \leq 1$ ), but with all due reserves.

One might reasonably wonder whether the use of more accurate expressions for the additive contact values  $g_{ij}^{\text{add}}$  might correct the inability of the theories examined in this paper to predict negative values of the virial coefficient  $B_{1122}$  for small size ratio  $\sigma_2/\sigma_1$  and large nonadditivity parameter  $\Delta$ . However, a closer analysis shows that this is not the case. According to Eq. (2.6),  $B_{1122} \propto \sigma_1^3 c_{22;11} + \sigma_2^3 c_{11;22} + 4\sigma_{12}^3 c_{12;12}$ . Therefore, at least one of the *nonadditive* second-order coefficients  $c_{22;11}$ ,  $c_{11;22}$ , and  $c_{12;12}$  must be negative if  $B_{1122} < 0$ . In contrast, the additive coefficients  $c_{ij;k\ell}^{\text{add}}$  are positive for any  $\sigma_2/\sigma_1$  and, as a consequence, all the *approximate* theories considered here predict positive values of  $c_{ij;k\ell}$  for  $\Delta > 0$ , as can be seen from Eqs. (3.1), (3.11), (3.12), (3.22), and (3.28).

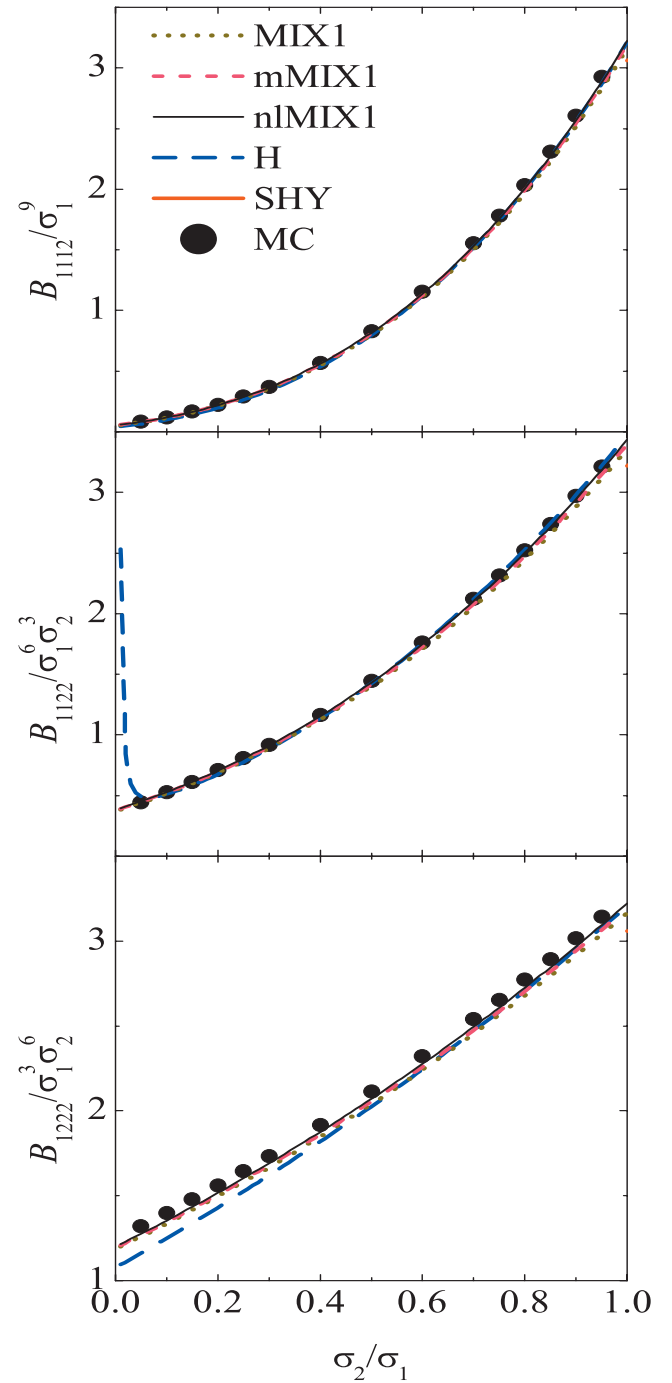
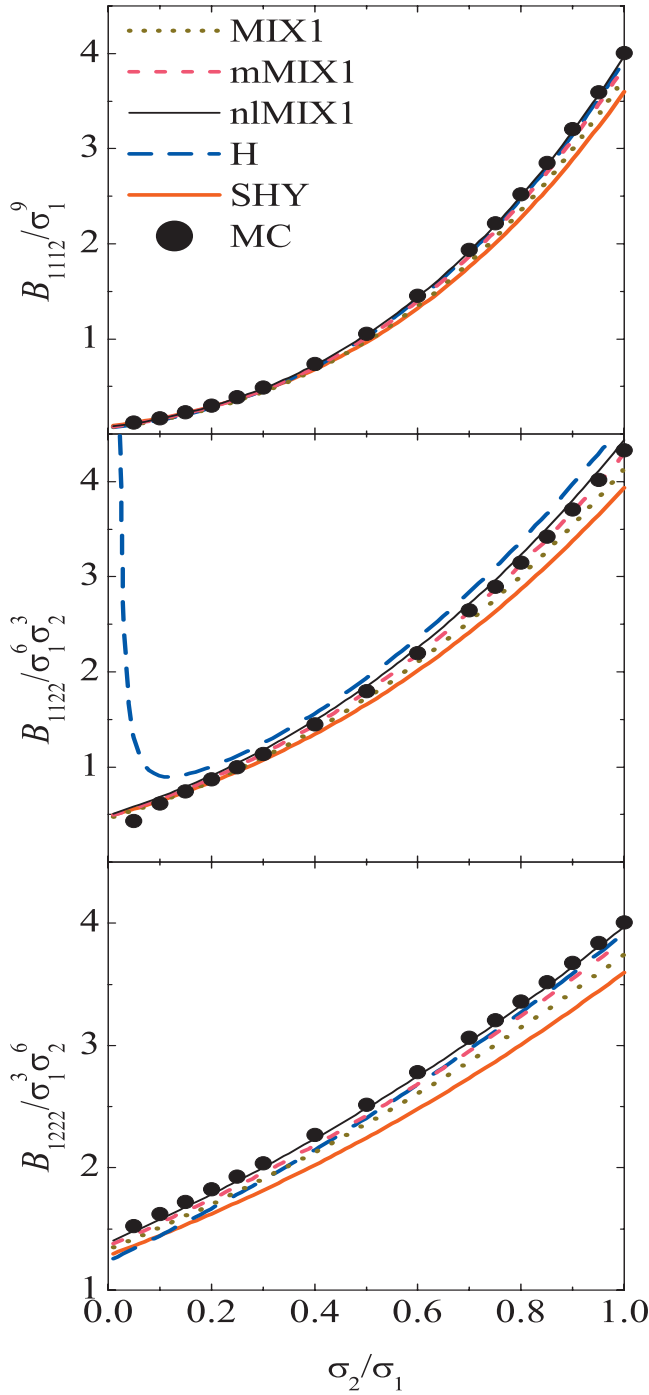
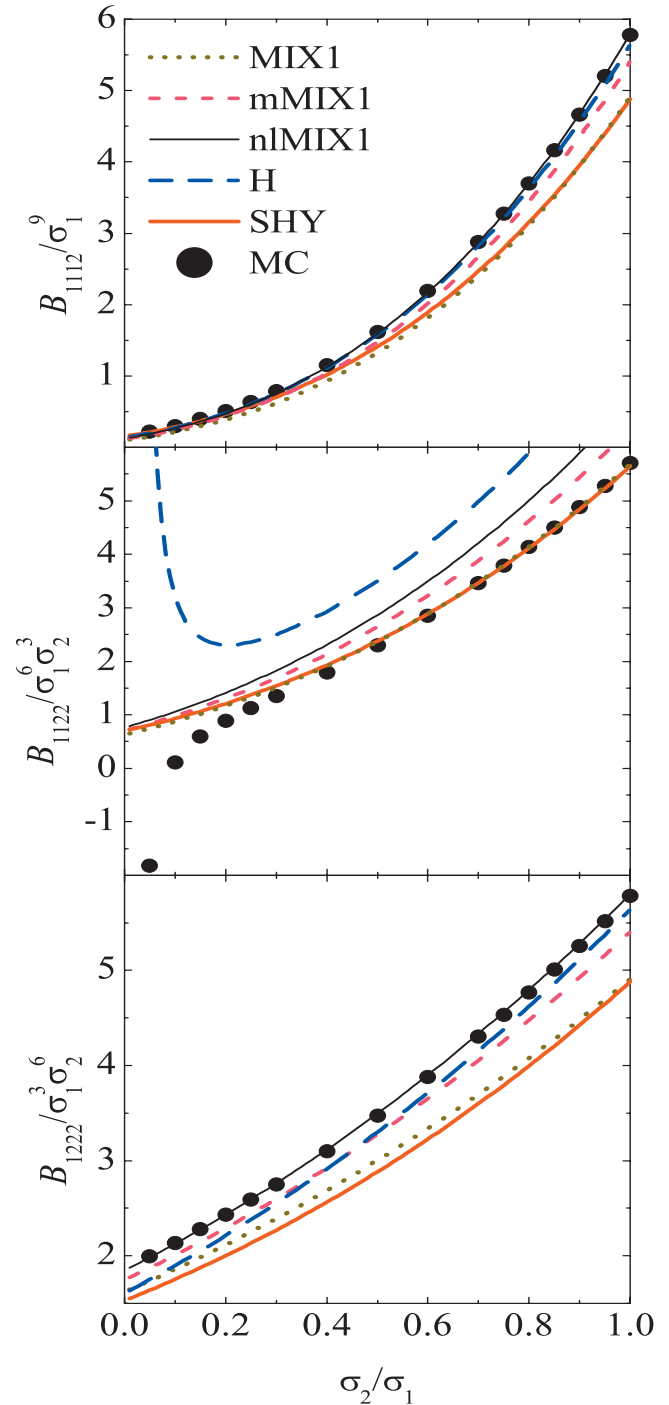


FIG. 1. Plot of the composition-independent fourth virial coefficients  $B_{1112}$ ,  $B_{1122}$ , and  $B_{1222}$  vs the size ratio  $\sigma_2/\sigma_1$  for a nonadditivity parameter  $\Delta = 0.05$ . The dotted lines correspond to the original MIX1 theory, Eq. (3.7), the short-dashed lines correspond to the mMIX1 theory, Eq. (3.7) with  $Y_{ij}^M \rightarrow Y_{ij}^{mM}$ , the thin solid lines correspond to the nlMIX1 theory, Eq. (3.34), the long-dashed lines correspond to Hamad's proposal, Eq. (3.20), and the thick solid lines correspond to the SHY proposal, Eq. (3.27). The symbols are Monte Carlo data from Ref. 17.

### B. Compressibility factor

To complement the above information on the virial coefficients, in Figs. 7–9 we present the results of our calculations of the compressibility factors of binary nonadditive hard-sphere mixtures and a comparison with available simulation data. Figure 7 displays the dependence of  $Z$  on the

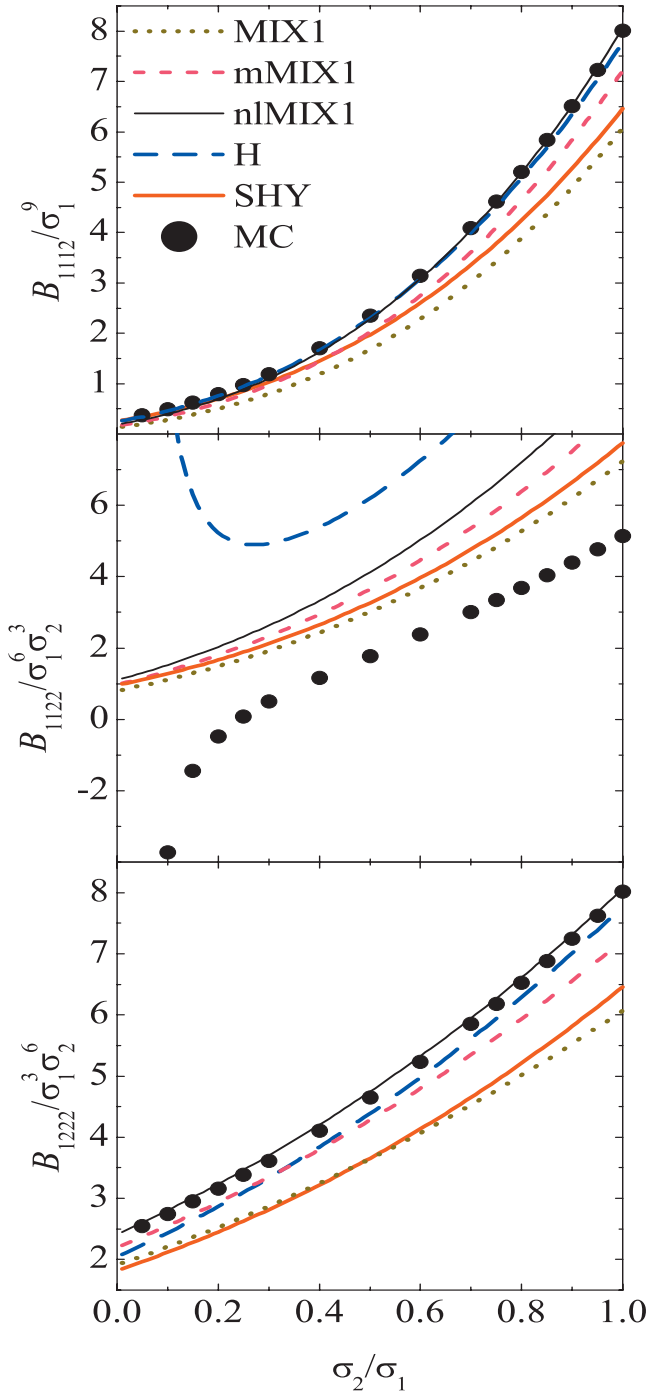
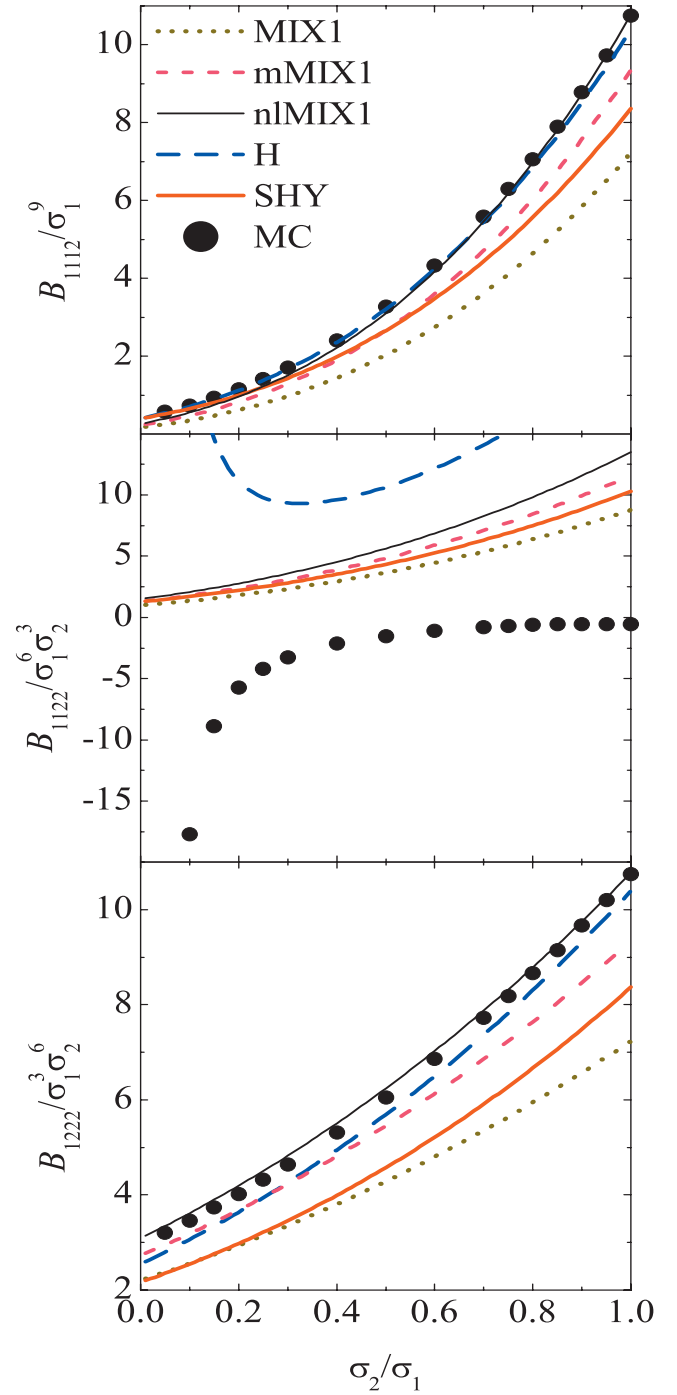
FIG. 2. Same as in Fig. 1, but for  $\Delta=0.1$ .FIG. 3. Same as in Fig. 1, but for  $\Delta=0.2$ .

nonadditivity parameter (both positive and negative) for a symmetric binary mixture at  $\eta=\pi/30\approx 0.105$  and two values of the mole fraction, namely,  $x_1=0.1$  and  $x_1=0.5$ . In this case, both the SHY proposal and the nLMIX1 theory provide the best agreement, but the mMIX1 theory also does a very good job. Hamad's proposal performs better at negative nonadditivities than at positive ones. As for the MIX1 theory, being linear in  $\Delta$ , it only captures the region of small  $|\Delta|$ .

The superiority of Hamad's theory for negative nonadditivities is confirmed by Fig. 8, which corresponds to the case of an equimolar *asymmetric* binary mixture with size ratio  $\sigma_2/\sigma_1=\frac{1}{3}$  and a packing fraction  $\eta=0.5$ . Here Hamad's ap-

proximation clearly outperforms all the rest. As a matter of fact, it becomes exact in the extreme limit  $\Delta\rightarrow-1$ .<sup>3</sup> A noteworthy feature is that in contrast to both the original MIX1 and the mMIX1 theories, the nLMIX1 theory at least captures correctly the qualitative behavior of the compressibility factor with the nonadditivity parameter for negative values and, in particular, the initial decay. This is remarkable in view of the fact that as discussed at the end of Sec. III, the nLMIX1 theory is not expected to hold if  $\Delta\leq-0.21$ .

Finally, in Fig. 9 we present the results obtained for the size ratio dependence of the compressibility factor for  $\eta=0.2$ , a positive nonadditivity  $\Delta=0.2$ , and two compositions.

FIG. 4. Same as in Fig. 1, but for  $\Delta=0.3$ .FIG. 5. Same as in Fig. 1, but for  $\Delta=0.4$ .

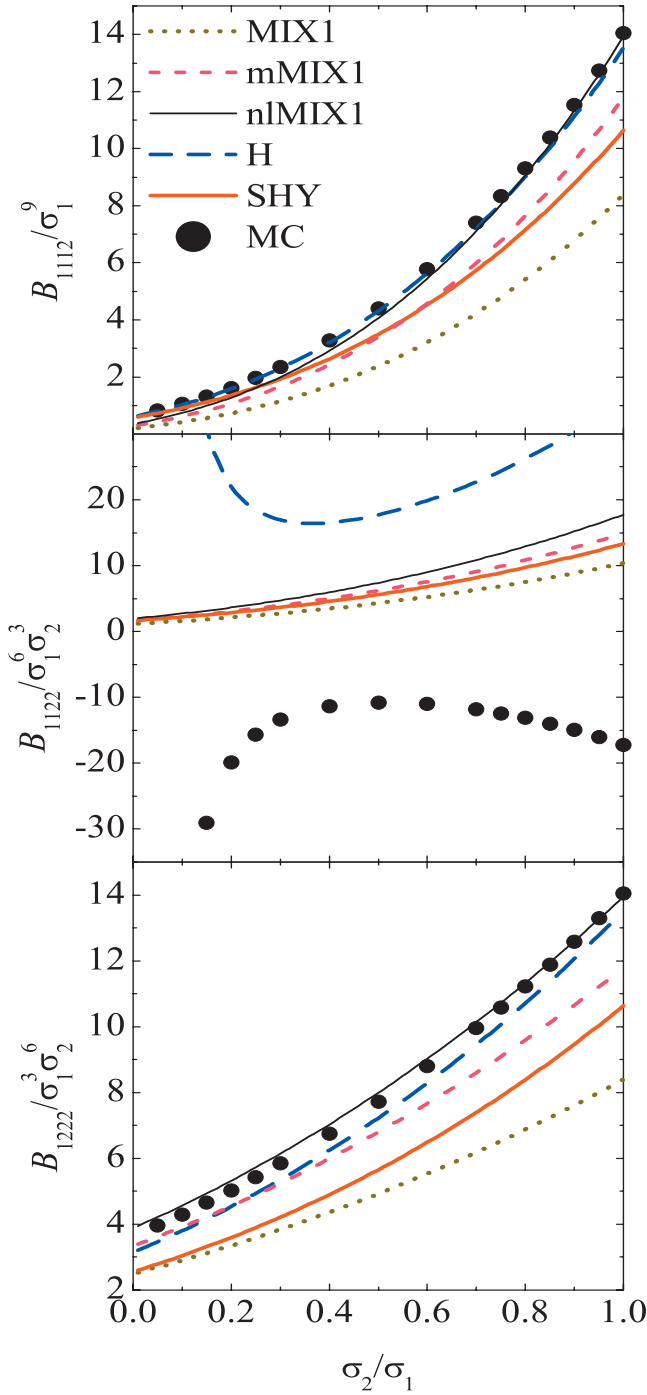
In agreement with the behavior observed in Fig. 7 for  $\Delta > 0$ , we see from Fig. 9 that the SHY is the superior theory also in the asymmetric case, although all the theories, with the exception of the MIX1, tend to coincide as the asymmetry increases. It is noteworthy that both the mMIX1 and nlMIX1 theories do a very reasonable job, better than Hamad's proposal.

### C. Demixing

The availability of analytical expressions for the Helmholtz free energy per particle  $a$  in all the previous theories [cf. Eqs. (3.4), (3.19), (3.25), and (3.32)] may be exploited to

address the problem of demixing in mixtures with positive nonadditivity. For simplicity, we will restrict ourselves here to binary mixtures. Since in these systems the temperature only plays the role of a scaling factor and a spinodal instability occurs, the mixture will phase separate into two liquid phases (I and II) of different composition  $x_1^I$  and  $x_1^{II}$ . For given size ratio  $\sigma_2/\sigma_1$  and nonadditivity  $\Delta$ , by equating the pressure ( $p^I=p^{II}$ ) and the two chemical potentials ( $\mu_1^I = \mu_1^{II}$ ,  $\mu_2^I = \mu_2^{II}$ ) of both phases, one may obtain  $\rho^I, \rho^{II}$ , and  $x_1^{II}$  as functions of  $x_1^I$  and thus derive the coexistence curve in the  $\rho$ - $x_1$  plane. The chemical potentials are defined by  $\mu_i = \partial(\rho a) / \partial \rho_i$ . In the binary case, this is equivalent to



FIG. 6. Same as in Fig. 1, but for  $\Delta=0.5$ .

$$\mu_1 = a + \frac{p}{\rho} + (1-x_1)a_x, \quad \mu_2 = a + \frac{p}{\rho} - x_1a_x, \quad (4.12)$$

where  $a_x \equiv (\partial a / \partial x_1)_\rho$ . Branches I and II of the coexistence line meet at the critical consolute point  $(\rho_c, x_{1c})$ , which can be determined by the two conditions,

$$0 = \left( a_{\rho\rho} + \frac{2}{\rho} a_\rho \right) a_{xx} - a_{xp}^2, \quad (4.13)$$

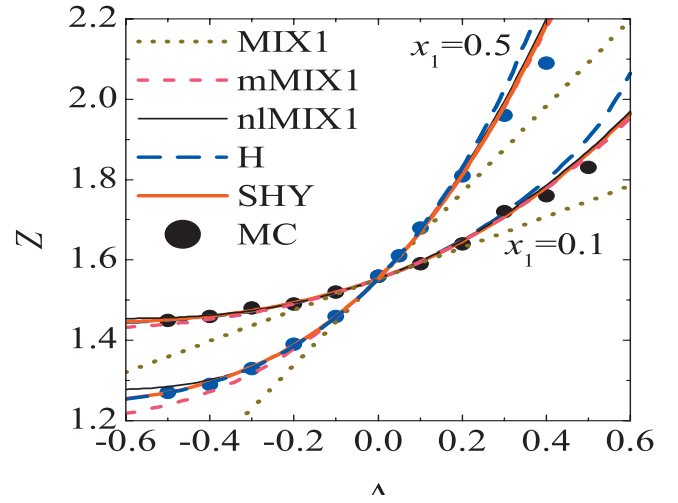


FIG. 7. Plot of the compressibility factor  $Z$  vs the nonadditivity parameter  $\Delta$  for a symmetric binary mixture of nonadditive hard spheres at  $\eta = \pi/30$  and two different compositions. The dotted lines correspond to the original MIX1 theory, Eq. (3.3), the short-dashed lines correspond to the mMIX1 theory, Eq. (3.3) with  $Y_{ij}^M \rightarrow Y_{ij}^{mM}$ , the thin solid lines correspond to the nLMIX1 theory, Eq. (3.31), the long-dashed lines correspond to Hamad's proposal, Eq. (3.18), and the thick solid lines correspond to the SHY proposal, Eq. (3.24). The symbols are results from Monte Carlo simulations (Refs. 10 and 11).

$$0 = a_{xxx} - 3a_{xx\rho} \frac{a_{xx}}{a_{xp}} + 3 \left( a_{x\rho\rho} + \frac{2}{\rho} a_{x\rho} \right) \left( \frac{a_{xx}}{a_{xp}} \right)^2 - \left( a_{\rho\rho\rho} + \frac{6}{\rho} a_{\rho\rho} + \frac{6}{\rho^2} a_\rho \right) \left( \frac{a_{xx}}{a_{xp}} \right)^3. \quad (4.14)$$

Here, as in Eq. (4.12), each subscript  $x$  or  $\rho$  represents a derivative with respect to  $x_1$  or  $\rho$ , respectively. For symmetric mixtures, the critical composition is fixed,  $x_{1c} = 0.5$ .

In Fig. 10 we display the behavior of the reduced critical

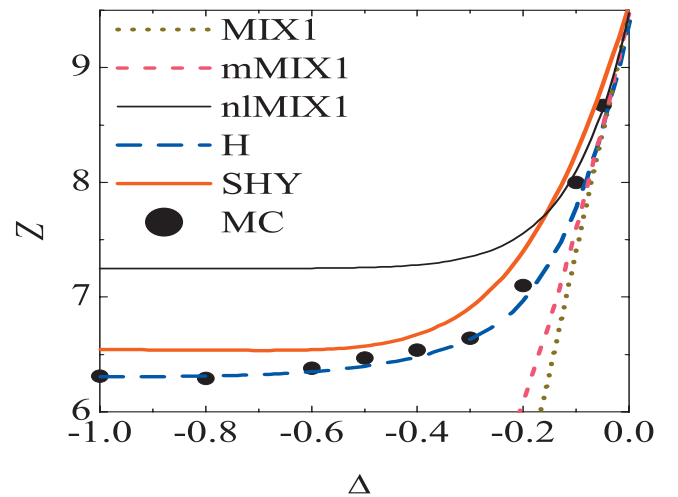


FIG. 8. Plot of the compressibility factor  $Z$  vs the nonadditivity parameter  $\Delta$  for an equimolar asymmetric binary mixture of nonadditive hard spheres with size ratio  $\sigma_2/\sigma_1 = \frac{1}{3}$  at  $\eta = 0.5$ . The dotted line corresponds to the original MIX1 theory, Eq. (3.3), the short-dashed line corresponds to the mMIX1 theory, Eq. (3.3) with  $Y_{ij}^M \rightarrow Y_{ij}^{mM}$ , the thin solid line corresponds to the nLMIX1 theory, Eq. (3.31), the long-dashed line corresponds to Hamad's proposal, Eq. (3.18), and the thick solid line corresponds to the SHY proposal, Eq. (3.24). The symbols are results from Monte Carlo simulations (Ref. 13).

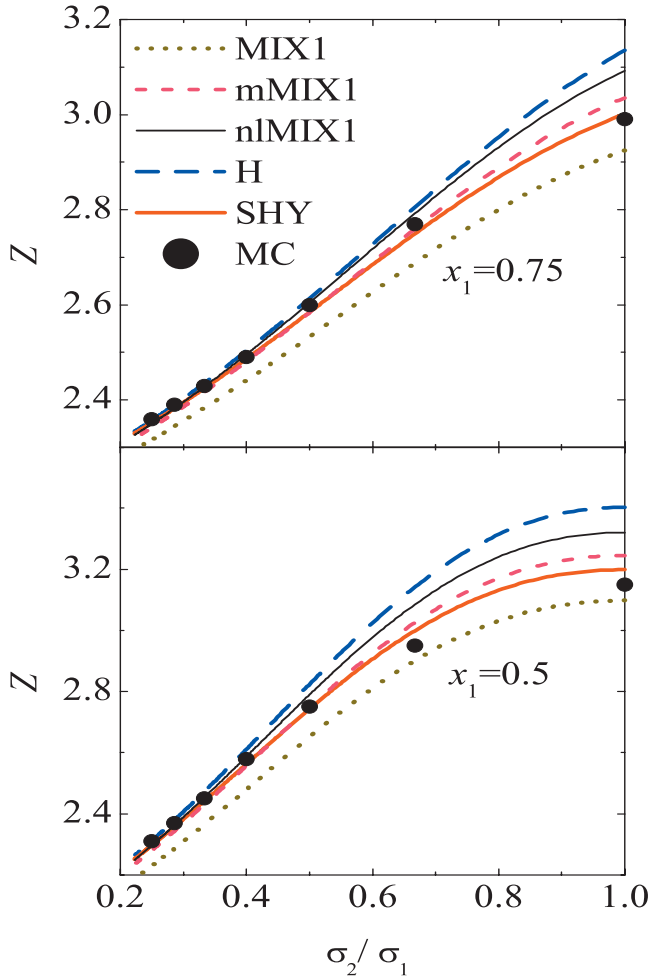


FIG. 9. Plot of the compressibility factor  $Z$  vs the size ratio  $\sigma_2/\sigma_1$  for binary mixtures of nonadditive hard spheres with  $\Delta=0.2$  and  $x_1=0.75$  (upper panel) and  $x_1=0.5$  (lower panel). The dotted lines correspond to the original MIX1 theory, Eq. (3.3), the short-dashed lines correspond to the mMIX1 theory, Eq. (3.3) with  $Y_{ij}^M \rightarrow Y_{ij}^{mM}$ , the thin solid lines correspond to the nLMIX1 theory, Eq. (3.31), the long-dashed lines correspond to Hamad's proposal, Eq. (3.18), and the thick solid lines correspond to the SHY proposal, Eq. (3.24). The symbols are results from Monte Carlo simulations (Ref. 13).

density  $\rho_c^* = \rho_c \sigma_{\text{eff}}^3$  in symmetric mixtures, where  $\sigma_{\text{eff}}^3 \equiv \sum_{i,j} x_i x_j \sigma_{ij}^3$ , as a function of the nonadditivity parameter  $\Delta$  for Hamad's theory, the SHY proposal, the mMIX1 and nLMIX1 theories, and the available simulation data. The original MIX1 theory has not been included since it has already been proved that it yields a poorer performance than Hamad's theory, which is the least accurate in this instance. Note that all theoretical results underestimate  $\rho_c^*$  and are very close to one another with perhaps a slightly better overall performance of the mMIX1 and the SHY. The use of the effective diameter  $\sigma_{\text{eff}}$  to define the reduced critical density in Fig. 10 is motivated by the fact that  $\rho_c^*$  is well defined for high nonadditivities, including the Widom–Rowlinson limit ( $\sigma_1 = \sigma_2 \ll \sigma_{12}$  or  $\Delta \rightarrow \infty$ ).

As far as the liquid-liquid coexistence curve is concerned, this may be represented in different thermodynamic planes. Here we have chosen the  $\rho \sigma_2^{3-x_1}$  and the  $p \sigma_2^3 / k_B T - x_1$  planes. Further, given the previous analysis concerning the comparison of the theoretical critical consolute points and simulation results, and the technical difficulties associated

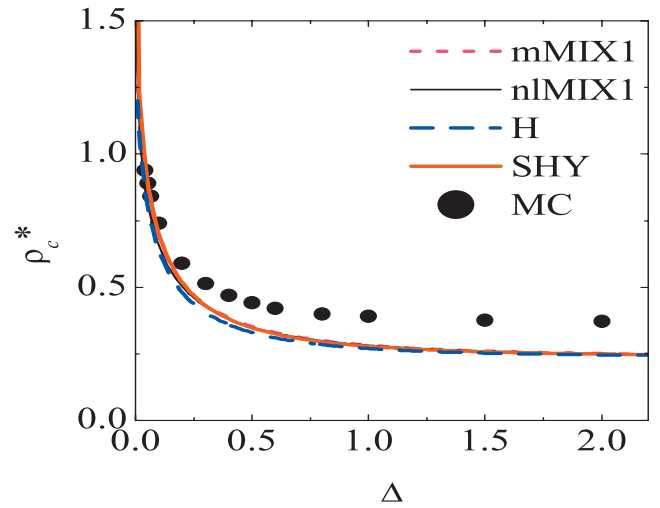


FIG. 10. Plot of the reduced critical density  $\rho_c^* = \rho_c \sigma_{\text{eff}}^3$  vs the nonadditivity parameter  $\Delta$  for symmetric binary mixtures of nonadditive hard spheres. The short-dashed line corresponds to the mMIX1 theory, the thin solid line corresponds to the nLMIX1 theory, the long-dashed line corresponds to Hamad's proposal, and the thick solid line corresponds to the SHY proposal. The symbols are results from Monte Carlo simulations (Refs. 25–27).

with the actual computation of the coexistence curves, only the results for the SHY and the mMIX1 and nLMIX1 theories will be presented. A comparison of available simulation results for liquid-liquid coexistence is done for both symmetric and asymmetric mixtures in Fig. 11, where the theoretical critical consolute points have also been included. Notice that the qualitative trends observed in the simulations are well captured by all the theoretical developments, but in all instances they tend to underestimate the actual values of the reduced pressure and the reduced density along the coexistence. In particular, all theories correctly predict that the demixing transition occurs for lower densities as the nonadditivity parameter increases. Moreover, at a fixed value of  $\Delta$  the coexistence densities (if measured in units of the diameter of the smaller spheres) decrease with increasing size asymmetry. Similar trends are observed for the pressure. On the quantitative side, particularly in the density versus composition plane, although not very accurate, the SHY outperforms the other theoretical approximations.

## V. CONCLUDING REMARKS

In this paper we have provided a self-contained presentation of different theoretical developments to describe the thermodynamic properties of nonadditive hard-core mixtures. In particular, complementing the effort initiated in our previous paper on this subject,<sup>3</sup> apart from repeating the SHY proposal and the extension of Hamad's approach to general dimensionalities, here we have provided extensions of the original MIX1 and Paricaud's modified MIX1 (mMIX1) theories valid for all  $d$ . We have introduced as well a new nonlinear extension of the MIX1 (nLMIX1) theory, also valid for arbitrary  $d$ . In all instances, explicit expressions have been provided for the contact values of the radial distribution functions, the compressibility factor, the Helmholtz free energy, and the second, third, and fourth virial coefficients. The expressions for  $g_{ij}(\rho)$  and  $Z(\rho)$  are given in

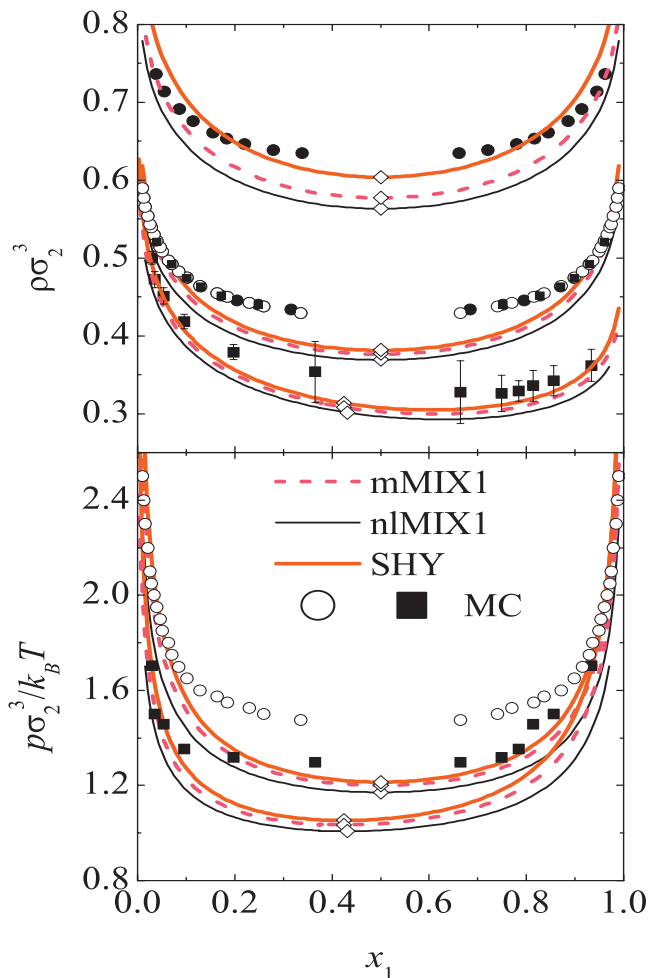


FIG. 11. Liquid-liquid coexistence curves for several binary mixtures of nonadditive hard spheres in the reduced density  $\rho\sigma_2^3$  vs composition  $x_1$  plane (top panel) and in the reduced pressure  $p\sigma_2^3/k_B T$  vs composition  $x_1$  plane (bottom panel). From top to bottom, the set of curves correspond to  $(\sigma_2/\sigma_1, \Delta) = (1, 0.1)$  (absent in the bottom panel),  $(1, 0.2)$ , and  $(5/6, 0.1818)$ . The short-dashed lines correspond to the mMIX1 theory, the thin solid lines correspond to the nLMIX1 theory, and the thick solid lines correspond to the SHY proposal. The diamonds indicate the locations of the respective critical consolute points. The other symbols are results from Monte Carlo simulations: Ref. 25 (filled circles), Ref. 28 (open circles), and Ref. 9 (filled squares).

terms of either  $g_{ij}^{\text{add}}(\rho)$  and  $Z^{\text{add}}(\rho)$  in the case of all the MIX1 theories, or in terms of  $g^{\text{pure}}(y)$ , or equivalently of  $Z^{\text{pure}}(y) = 1 + 2^{d-1}y g^{\text{pure}}(y)$ , in the cases of Hamad's and the SHY approximations. For the sake of illustration and restricting to three-dimensional systems ( $d=3$ ), we have taken as input the BMCSL equation of state for  $Z^{\text{add}}(\rho)$  and the BGHLL contact values for  $g_{ij}^{\text{add}}(\rho)$  in the MIX1 theories, and the CS equation of state for  $Z^{\text{pure}}(y)$  in the SHY and Hamad's proposals.

To our knowledge, the idea of starting from the contact values of the radial distribution functions in the case of the MIX1 theories has not been considered before. This allowed us to construct the nonlinear extension. Of course, while in the case of mixtures the compressibility factor is determined uniquely once the contact values of the radial distribution function are given, the reciprocal is not true. Hence, the expressions we have provided for these contact values are a further contribution of this work.

We have carried out three kinds of comparison between

the five theories and "exact" numerical results. First, the theoretical predictions of the composition-independent fourth virial coefficients have been tested against new available Monte Carlo data.<sup>17</sup> In the cases of  $B_{1112}$  and  $B_{1222}$ , the best overall agreement with the Monte Carlo values are obtained with the nLMIX1 theory, followed by Hamad's proposal. As for  $B_{1122}$ , none of the theories does well at high asymmetry and nonadditivity, the discrepancies being especially important in the case of Hamad's approximation.

As is well known, the first few virial coefficients are relevant to the equation of state in the low-density regime but not generally beyond it. Thus, in order to test the theoretical approaches at finite densities, we have made use of available simulation data for the compressibility factor.<sup>10,11,13</sup> The emerging scenario is that Hamad's approximation is excellent for negative nonadditivities, while the SHY proposal is the preferable one for positive nonadditivities.

Within the limited set of compressibility factors that we have analyzed, it is fair to say that the new nLMIX1 theory proposed in this paper is rather satisfactory and seems to be a good compromise between accuracy and simplicity. Further assessment of this assertion is precluded at this stage due to the scarcity of the data. Therefore, one of our hopes is that the present paper may encourage more work on the subject.

Finally, the critical behavior and liquid-liquid coexistence of nonadditive hard-sphere mixtures with positive nonadditivity have been examined. While the quantitative agreement is not satisfactory, all theories seem to capture correctly the qualitative trends obtained in the simulation. In this case our original SHY proposal gives the best performance, but again the limited availability of data prevents us from carrying out a more thorough analysis. Once more we hope that our findings may lead to the further needed work on this matter.

## ACKNOWLEDGMENTS

This work has been supported by the Ministerio de Educación y Ciencia (Spain) through Grant No. FIS2007-60977 (partially financed by FEDER funds).

- <sup>1</sup>B. Widom and J. S. Rowlinson, *J. Chem. Phys.* **52**, 1670 (1970).
- <sup>2</sup>S. Asakura and F. Oosawa, *J. Chem. Phys.* **22**, 1255 (1954); *J. Polym. Sci., Polym. Phys. Ed.* **33**, 183 (1958).
- <sup>3</sup>A. Santos, M. López de Haro, and S. B. Yuste, *J. Chem. Phys.* **122**, 024514 (2005).
- <sup>4</sup>A. Santos, S. B. Yuste, and M. López de Haro, *Mol. Phys.* **96**, 1 (1999).
- <sup>5</sup>E. Z. Hamad, *J. Chem. Phys.* **101**, 10195 (1994).
- <sup>6</sup>E. Z. Hamad, *J. Chem. Phys.* **105**, 3222 (1996).
- <sup>7</sup>E. Z. Hamad, *J. Chem. Phys.* **105**, 3229 (1996).
- <sup>8</sup>E. Z. Hamad and G. O. Yahaya, *Fluid Phase Equilib.* **168**, 59 (2000).
- <sup>9</sup>M. Rovere and G. Pastore, *J. Phys.: Condens. Matter* **6**, A163 (1994).
- <sup>10</sup>J. Jung, M. S. Jhon, and F. H. Ree, *J. Chem. Phys.* **100**, 528 (1994).
- <sup>11</sup>J. Jung, M. S. Jhon, and F. H. Ree, *J. Chem. Phys.* **100**, 9064 (1994).
- <sup>12</sup>J. Jung, M. S. Jhon, and F. H. Ree, *J. Chem. Phys.* **102**, 1349 (1995).
- <sup>13</sup>E. Z. Hamad, *Mol. Phys.* **91**, 371 (1997).
- <sup>14</sup>F. Saija, G. Fiumara, and P. V. Giaquinta, *J. Chem. Phys.* **108**, 9098 (1998).
- <sup>15</sup>A. Yu. Vlasov and A. J. Masters, *Fluid Phase Equilib.* **212**, 183 (2003).
- <sup>16</sup>T. W. Melnyk and B. L. Sawford, *Mol. Phys.* **29**, 891 (1975).
- <sup>17</sup>G. Pellicane, C. Caccamo, P. V. Giaquinta, and F. Saija, *J. Phys. Chem. B* **111**, 4503 (2007).
- <sup>18</sup>P. Paricaud, *Phys. Rev. E* **78**, 021202 (2008).
- <sup>19</sup>T. Boublík, *J. Chem. Phys.* **53**, 471 (1970).

- <sup>20</sup>G. A. Mansoori, N. F. Carnahan, K. E. Starling, and J. T. W. Leland, *J. Chem. Phys.* **54**, 1523 (1971).
- <sup>21</sup>E. W. Grundke and D. Henderson, *Mol. Phys.* **24**, 269 (1972).
- <sup>22</sup>L. L. Lee and D. Levesque, *Mol. Phys.* **26**, 1351 (1973).
- <sup>23</sup>N. F. Carnahan and K. E. Starling, *J. Chem. Phys.* **51**, 635 (1969).
- <sup>24</sup>We note that Tables 4 and 6 of Ref. 17 contain some errata. The correct entries in the original notation should be as follows [G. Pellicane and F. Saija, private communication (2009)]:  $D_{1122}=-2.0688(2)\times 10^{-3}$  for  $q=0.05$  and  $\Delta=0.3$ ;  $D_{1122}=1.888(5)$  for  $q=0.8$  and  $\Delta=0.3$ ;  $D_{1122}=-5.6318(3)\times 10^{-2}$  for  $q=0.1$  and  $\Delta=0.5$ ;  $D_{1112}=9.314(9)$  for  $q=0.8$  and  $\Delta=0.5$ .
- <sup>25</sup>K. Jagannathan and A. Yethiraj, *J. Chem. Phys.* **118**, 7907 (2003).
- <sup>26</sup>W. T. Gózdź, *J. Chem. Phys.* **119**, 3309 (2003).
- <sup>27</sup>A. Buhot, *J. Chem. Phys.* **122**, 024105 (2005).
- <sup>28</sup>E. Lomba, M. Alvarez, L. L. Lee, and N. G. Almarza, *J. Chem. Phys.* **104**, 4180 (1996).