

Equation of state for fluid mixtures of hard spheres and linear homonuclear fused hard spheres

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This paper develops a theoretically based equation of state for fluid mixtures consisting of hard spheres and linear homonuclear fused hard spheres. The procedure is based on the equation of state previously developed for monocomponent athermal fluids. The equation of state only requires two parameters, namely the averaged effective molecular volume of the molecules in the mixture and the corresponding effective nonsphericity parameter. These parameters can be obtained from the geometry of the molecules forming the mixture. The results are in excellent agreement with simulation data and compare favorably with those obtained from other theories for athermal fluid mixtures. [S1063-651X(98)12508-4]

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I. INTRODUCTION

For several decades, athermal fluids and their mixtures have been the subject of a great deal of research from a theoretical viewpoint as well as with computer simulation. This is because these fluids have many properties in common with real fluids but are simpler to understand and deal with. Moreover, one of the most fruitful approaches for studying fluids with more realistic intermolecular forces is by means of perturbation theories. These theories consider attractive forces as a perturbation of repulsive ones, which in turn are often modeled through infinitely steep repulsive potentials. To do so, the thermodynamic properties of the real fluid are usually expanded in power series of the inverse of the absolute temperature around the infinite temperature limit. At this limit, real molecular fluids behave like athermal fluids, so that we must first know the properties of a suitable reference athermal fluid. The most convenient choice is one whose molecules are similar in shape to those of the real fluid. The same is true for fluid mixtures.

Although the Percus-Yevick equation for a mixture of hard spheres was solved [1] in 1964, it was not until the early 1970's that a sufficiently accurate equation of state was developed [2,3] for this mixture. This can be considered the starting point of an increasing interest in athermal fluid mixtures. Nearly at the same time, the scaled particle theory (SPT) was developed [4] for hard convex body (HCB) fluid mixtures. The SPT equation of state for mixtures was further improved in several different ways [5,6] on a semiempirical basis.

About one decade later, a theory for chain molecular fluid mixtures, thermodynamic perturbation theory (TPT), was developed [7,8]. Since then, advances in this field have speeded up. In the 1990's, equations of state for athermal fluid mixtures have been derived from Percus-Yevick (PY) theory [9,10], bonded hard-sphere (BHS) theory [11], generalized Flory (GF) theory [12], and generalized Flory dimer (GFD) theory [13].

At present, all the above-mentioned theories suffer from some limitations. Those based on SPT are not expected to be

accurate for mixtures of highly asymmetrical molecules [11]. Moreover, the nonsphericity parameter for large asymmetrical polyatomic molecules must be calculated numerically, which means that analytical equations of state cannot be obtained for those fluids and their mixtures. TPT and GF or GFD theories apply to flexible chains, but not to rigid molecules. Perhaps one of the most successful theories for mixtures is the BHS theory, which is analytical, accurate, and applicable to both rigid and flexible molecules. However, it only applies to fluids consisting of fused hard sphere (FHS) molecules, but not to pure fluids or mixtures of convex molecules.

In a previous paper [14], an accurate equation of state for hard convex body (HCB) fluid mixtures was developed. It was based on the equation of state derived earlier [15] for pure HCB fluids. In the present paper we will derive an equation of state for mixtures of hard spheres and linear homonuclear fused hard spheres. Formally, the generalization from the equation of state of HCB fluid mixtures to that for mixtures containing nonconvex molecules is similar to the generalization from the equation of state of pure HCB fluids to that for pure FHS fluids [16]. However, for mixtures it is necessary to derive the required expressions to determine the effective molecular volumes and nonsphericity parameters for the mixtures. These expressions depend on the geometrical characteristics of the molecules that form the mixture.

Section II summarizes the derivation of the equation of state for pure hard-body fluids. In Sec. III the equation of state for fluid mixtures consisting of convex molecules is derived and further generalized to mixtures of nonconvex molecules. In Sec. IV, expressions are obtained that allow us to determine the parameters involved in the equation of state of mixtures of spheres and linear homonuclear fused hard spheres. Finally, in Sec. V, we compare the results with those from other theories and with simulation data, and discuss the findings.

II. EQUATION OF STATE FOR PURE HARD-BODY FLUIDS

Consider a one-component fluid at number density ρ consisting of HCB molecules. Let $g^{\text{av}}(0)$ denote the contact value of the pair correlation function, and σ^{av} the average

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distance between the centers of a pair of molecules projected onto the normal to the surface at the contact point, with both averages being taken over all possible orientations of the pair of molecules. Let S_{1+2} be the surface area of the body defined by the center of molecule 2 moving around molecule 1 while the two molecules remain in contact. Then, the compressibility factor can be expressed [17] in the form

$$Z^{\text{HCB}} = \frac{PV}{NkT} = 1 + \frac{1}{6} \rho S_{1+2} \sigma^{\text{av}} g^{\text{av}}(0). \quad (1)$$

For identical molecules, $S_{1+2} = 2S + 8\pi R^2$, where S is the surface of the molecule and R the $(1/4\pi)$ multiple of the mean curvature integral.

As a particular case for hard spheres of diameter σ , expression (1) gives

$$Z^{\text{HS}} = 1 + \frac{2}{3} \pi \rho \sigma^3 g^{\text{HS}}(0). \quad (2)$$

For a given density ρ , if we consider spheres with volume $v = (\pi/6)\sigma^3$ equal to those of the HCB molecules, from Eqs. (1) and (2), we easily arrive at

$$\frac{Z^{\text{HCB}} - 1}{Z^{\text{HS}} - 1} = \frac{1}{2} \left(\alpha + \frac{\frac{4}{3} \pi R^3}{v} \right) \frac{\sigma^{\text{av}} g^{\text{av}}(0)}{2R g^{\text{HS}}(0)}, \quad (3)$$

where the nonsphericity parameter or shape factor

$$\alpha = \frac{RS}{3v} \quad (4)$$

has been introduced.

It has been shown [15] that the approximations

$$\frac{\sigma^{\text{av}} g^{\text{av}}(0)}{2R g^{\text{HS}}(0)} \approx 1 \quad (5)$$

and

$$\frac{1}{2} \left(\alpha + \frac{\frac{4}{3} \pi R^3}{v} \right) \approx \alpha, \quad (6)$$

which are exact for hard spheres, that is, for $\alpha = 1$, also hold very accurately for nonspherical HCB molecules with moderate values of α . Moreover, the small errors introduced by these two approximations largely cancel each other out when they are put into Eq. (3).

Combining Eqs. (3), (5), and (6), we obtain the final form of the equation of state for HCB fluids:

$$Z^{\text{HCB}} = 1 + \alpha(Z^{\text{HS}} - 1), \quad (7)$$

which showed [15] very good agreement with simulation data, when the Carnahan-Starling equation [18]

$$Z^{\text{CS}} = \frac{1 + y + y^2 - y^3}{(1 - y)^3}, \quad (8)$$

where $y = \rho v$ is the packing fraction, was used for Z^{HS} .

Equation of state (7) was extended [16,19] to FHS fluids by taking into account the fact that, for them, the volume that

a molecule excludes to any point of another molecule is greater than the molecular volume v , as Fig. 1 shows. Therefore, we had to introduce an effective molecular volume v^{eff} , and subsequently, an effective packing fraction y^{eff} , instead of the molecular volume v and the packing fraction y . Moreover, as the nonsphericity parameter cannot be obtained from Eq. (4) for nonconvex molecules, a definition based [20] on the effective molecular volume was used. If this shape factor is denoted by α^{eff} , the resulting equation of state has the form

$$Z^{\text{FHS}} = 1 + \alpha^{\text{eff}}[Z^{\text{CS}}(y^{\text{eff}}) - 1]. \quad (9)$$

This equation was shown to provide very good agreement with simulation data for both homonuclear [16] and heteronuclear [19] FHS fluids.

III. EQUATION OF STATE FOR HARD-BODY FLUID MIXTURES

Let us first consider mixtures of HCB molecules. The generalization of expression (1) for these fluid mixtures is

$$Z_{\text{mix}}^{\text{HCB}} = 1 + \frac{1}{6} \sum_{i,j} \rho x_i x_j S_{i+j} \sigma_{ij}^{\text{av}} g_{ij}^{\text{av}}(0), \quad (10)$$

where x_i and x_j are the mole fractions of type i and j molecules in the mixture. If we assume that the procedure outlined in the preceding section can be applied to each term of the sum on the right-hand side, we will obtain

$$Z_{\text{mix}}^{\text{HCB}} = 1 + \sum_{i,j} \alpha_{ij} [Z^{\text{CS}}(y_{ij}) - 1], \quad (11)$$

where $y_{ij} = \rho x_i x_j v_{ij}$, with $v_{ij} = (v_{ii} + v_{jj})/2$.

If we consider separately each of the pure fluids forming the mixture, from Eq. (7), we will have

$$\frac{Z_{ii} - 1}{\alpha_{ii}} = Z^{\text{CS}}(y_{ii}) - 1, \quad (12)$$

where the right-hand side is the excess compressibility factor of a pure fluid of hard spheres, each of them with the same volume as the HCB molecule. From Eq. (12), the excess compressibility factor of a pure HCB fluid forming the mixture, when scaled by means of the shape factor, reduces to that of a pure HS fluid. Therefore, mixing all those ‘‘scaled’’ fluids together we will obtain a hard-sphere fluid mixture. So that, introducing a suitable nonsphericity parameter α_{mix} for the mixture, we can put

$$\frac{Z_{\text{mix}}^{\text{HCB}} - 1}{\alpha_{\text{mix}}} = Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}}) - 1. \quad (13)$$

Here, $Z_{\text{mix}}^{\text{HS}}$ is the compressibility factor of a mixture of hard spheres, $y_{\text{mix}} = \rho v_{\text{mix}}$ is the packing fraction of the mixture, and

$$v_{\text{mix}} = \sum_{i,j} x_i x_j v_{ij} \quad (14)$$

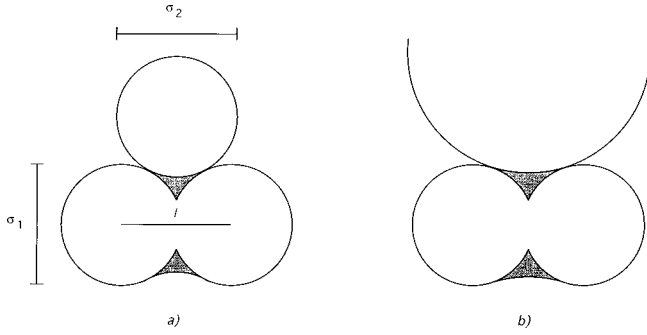


FIG. 1. Shaded area represents the difference between effective and real molecular volume of a hard dumbbell (a) as “seen” by a hard sphere of the same diameter as each of the spheres of the dumbbell and (b) as “seen” by a bigger sphere.

is the averaged volume of a molecule of the mixture either of HCB molecules or of hard spheres, because the spheres of species i in the HS mixture have the same volume and the same mole fraction as molecules of species i in the HCB mixture.

On the other hand, the low density expansion of Eq. (11) up to first order gives

$$\begin{aligned} Z_{\text{mix}}^{\text{HCB}} - 1 &\approx \sum_{i,j} \alpha_{ij} 4y_{ij} = \sum_{i,j} \alpha_{ij} \frac{v_{ij}}{v_{\text{mix}}} 4y_{ij} \frac{v_{\text{mix}}}{v_{ij}} \\ &= 4y_{\text{mix}} \sum_{i,j} \alpha_{ij} x_i x_j \frac{v_{ij}}{v_{\text{mix}}}. \end{aligned} \quad (15)$$

As a particular case, for a mixture of hard spheres, taking $\alpha_{ij} = 1$ for every i and j we have

$$Z_{\text{mix}}^{\text{HS}} - 1 \approx 4y_{\text{mix}} \sum_{i,j} x_i x_j \frac{v_{ij}}{v_{\text{mix}}}. \quad (16)$$

If we take into account expression (14), the preceding equation reduces to

$$Z_{\text{mix}}^{\text{HS}} - 1 \approx 4y_{\text{mix}}. \quad (17)$$

Introducing this result into Eq. (13) we obtain

$$Z_{\text{mix}}^{\text{HCB}} - 1 \approx \alpha_{\text{mix}} 4y_{\text{mix}}, \quad (18)$$

so that

$$\alpha_{\text{mix}} = \sum_{i,j} x_i x_j \alpha_{ij} \frac{v_{ij}}{v_{\text{mix}}}. \quad (19)$$

Although expression (19) has been derived from a low density expansion, it should hold at any density because α_{mix} is a geometrical parameter that depends on the shape of the molecules forming the mixture but not on density.

If a procedure similar to that used to derive Eq. (18) were applicable for higher order terms in the expansion, we would arrive at

$$Z_{\text{mix}}^{\text{HS}} - 1 \approx 4y_{\text{mix}} + 10y_{\text{mix}}^2 + 18y_{\text{mix}}^3 + \dots = Z^{\text{CS}}(y_{\text{mix}}) - 1, \quad (20)$$

that is, we would obtain the equation of state of the HS mixture as the CS equation of state of a pure fluid having the same packing fraction as the mixture. Although this seems reasonable, the fact is that if each of the pure HS fluids obeys the Carnahan-Starling equation, the compressibility factor for the m -component hard-sphere mixture is [2,3]

$$Z_{\text{mix}}^{\text{HS}} = \frac{6}{\pi\rho} \left(\frac{\zeta_0}{1-\zeta_3} + \frac{3\zeta_1\zeta_2}{(1-\zeta_3)^2} + \frac{3\zeta_2^3}{(1-\zeta_3)^3} - \frac{\zeta_3\zeta_2^3}{(1-\zeta_3)^3} \right), \quad (21)$$

where

$$\zeta_l = \frac{\pi\rho}{6} \sum_i x_i (\sigma_i)^l. \quad (22)$$

In the latter equation ρ is the total number density and σ_i is the diameter of spheres of component i , so that ζ_3 represents the packing fraction y_{mix} of the mixture. If we take into account that $\rho = y_{\text{mix}}/v_{\text{mix}}$, it is clear that the ζ_l can be expressed in terms of y_{mix} , and the same is true for expression (21). If we do so, we will arrive at an expression that does not coincide with the CS equation. In particular, at low enough densities, instead of Eq. (18) we will have

$$Z_{\text{mix}}^{\text{HS}} - 1 \approx B_{\text{mix}}^{\text{HS}} y_{\text{mix}}, \quad (23)$$

where $B_{\text{mix}}^{\text{HS}}$ is the second virial coefficient of the HS mixture, which, from Eq. (21), is given by

$$B_{\text{mix}}^{\text{HS}} = \frac{\sum_{i,j} x_i x_j v_{ij} + 3 \sum_{i,j} x_i x_j v_i^{1/3} v_j^{2/3}}{\sum_{i,j} x_i x_j v_{ij}} = 1 + 3\alpha_{\text{mix}}^{\text{HS}}, \quad (24)$$

where $\alpha_{\text{mix}}^{\text{HS}}$ is a sort of shape factor for the HS mixture, which in general differs from unity, unlike what occurs for the pure HS fluid. Therefore, from Eq. (13), the compressibility factor of HCB fluid mixtures can be expressed

$$Z_{\text{mix}}^{\text{HCB}} = 1 + \alpha_{\text{mix}} [Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}}) - 1], \quad (25)$$

together with Eqs. (14) and (19), and $Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}})$ given by Eq. (21).

Note that, for a binary mixture of spheres with different sizes, $\alpha_{11} = 1$ and $\alpha_{22} = 1$. This gives $\alpha_{12} = 1$ and, from Eq. (19), $\alpha_{\text{mix}} = 1$, and Eq. (25) is reduced to the equation of state (21) for the hard sphere fluid mixture. Therefore, although expression (19) has the form of a mixing rule, it is not exactly so, because it is not used in combination with the pure HCB fluid equation of state to obtain the equation of state of the HCB fluid mixture. α_{mix} , as given by Eq. (19), scales the excess compressibility factor of a *hard sphere fluid mixture* to obtain that corresponding to the HCB fluid mixture.

Equation (25), which showed [14] very good agreement with simulation data for binary mixtures of hard spheres with hard spherocylinders, can be readily extended to mixtures having nonconvex molecules. To do so, we must introduce an effective packing fraction of the mixture $y_{\text{mix}}^{\text{eff}} = \rho v_{\text{mix}}^{\text{eff}}$, where $v_{\text{mix}}^{\text{eff}}$ is the effective molecular volume of the mixture

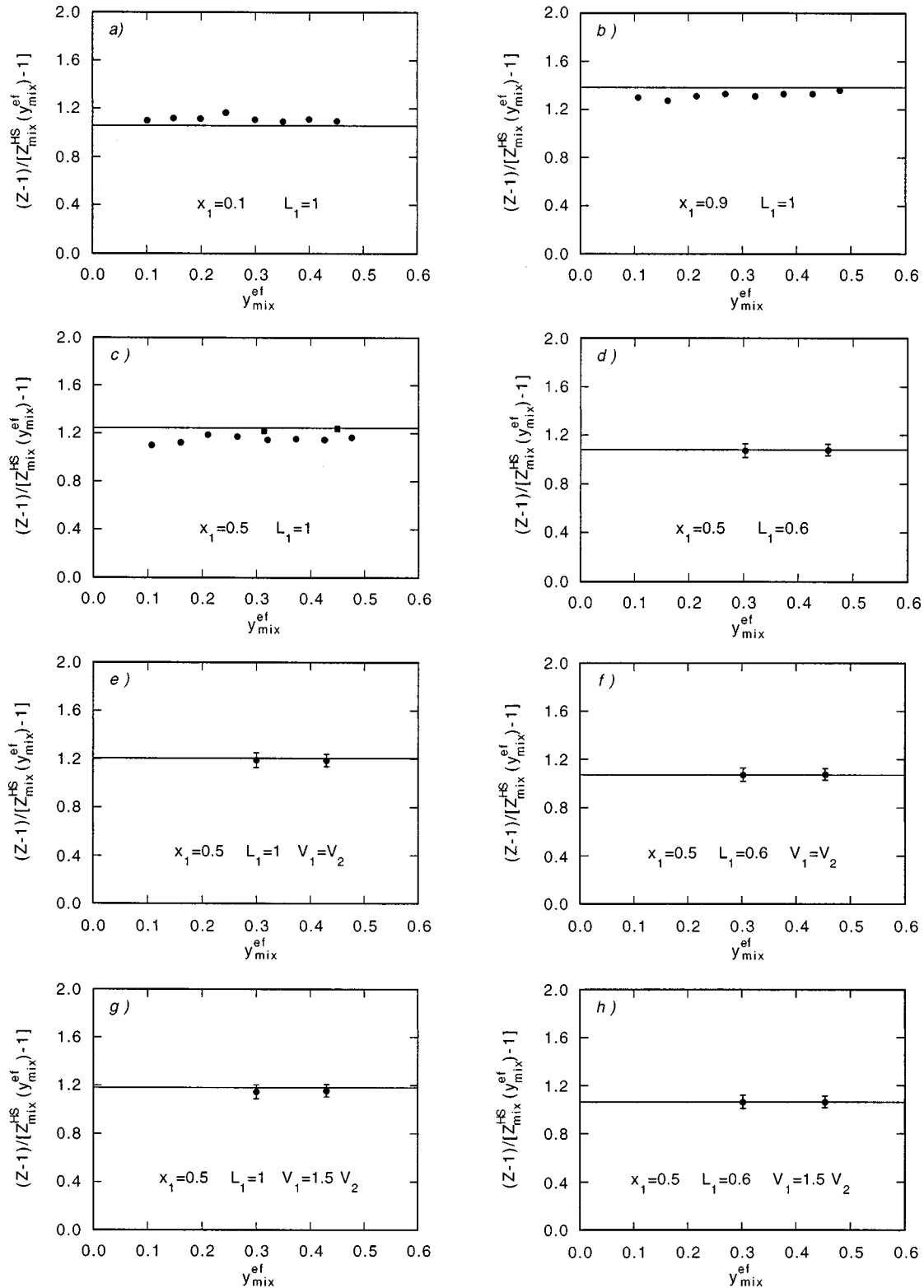


FIG. 2. Value of the ratio $(Z_{\text{mix}}^{\text{HB}} - 1)/[Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}}^{\text{eff}}) - 1]$ for different HMD-HS mixtures as a function of the effective packing fraction $y_{\text{mix}}^{\text{eff}}$ of the mixture. Points: results from simulation data from Refs. [21] (circles) and [22] (squares). Continuous line: Eq. (26). Error bars account for the inaccuracy ΔZ in the simulation data, when known, according to $\Delta Z/[Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}}^{\text{eff}}) - 1]$.

and the effective nonsphericity parameter α_{eff} , for the same reasons pointed out within the context of pure FHS fluids. Thus, we will have

$$Z_{\text{mix}}^{\text{HB}} = 1 + \alpha_{\text{mix}}^{\text{eff}}[Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}}^{\text{eff}}) - 1], \quad (26)$$

where

$$y_{\text{mix}}^{\text{eff}} = \sum_{i,j} x_i x_j y_{ij}^{\text{eff}} \quad (27)$$

and

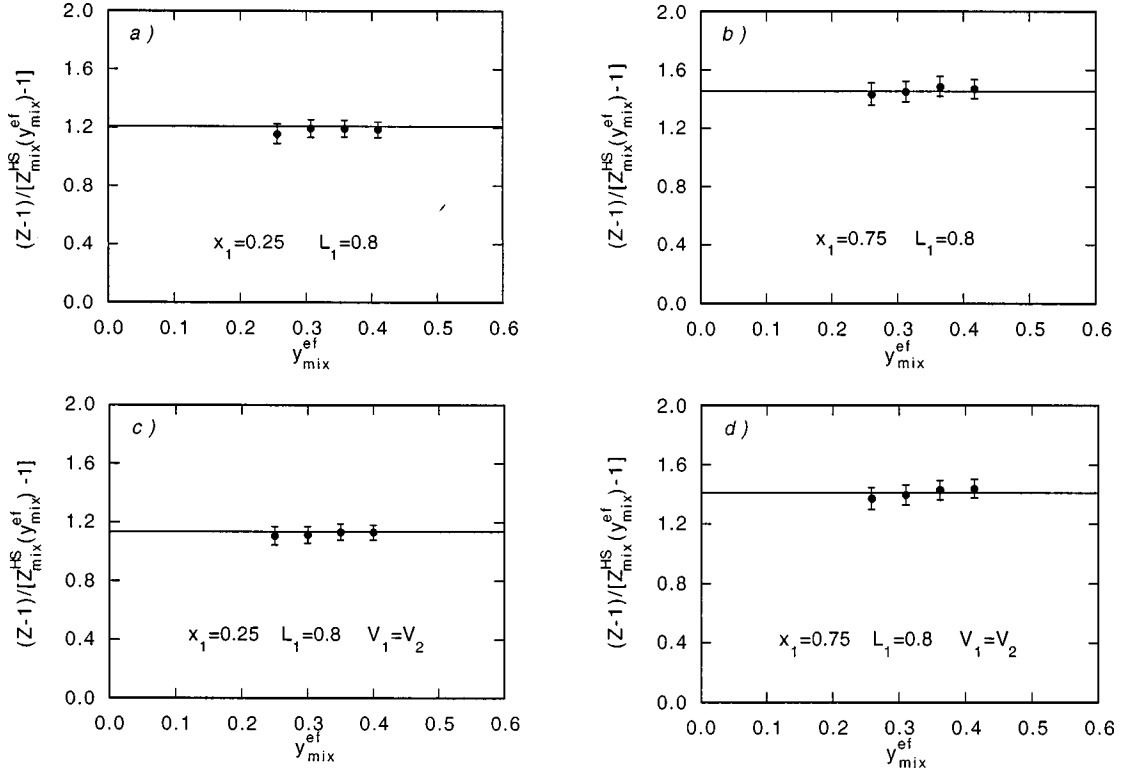


FIG. 3. As in Fig. 2 for HMLST-HS mixtures. Points: simulation data from Ref. [23].

$$\alpha_{\text{mix}}^{\text{eff}} = \sum_{i,j} x_i x_j \alpha_{ij}^{\text{eff}} \frac{v_{ij}^{\text{eff}}}{v_{\text{mix}}^{\text{eff}}}, \quad (28)$$

with

$$v_{\text{mix}}^{\text{eff}} = \sum_{i,j} x_i x_j v_{ij}^{\text{eff}}, \quad (29)$$

and it is clear that $y_{\text{mix}}^{\text{eff}} = \rho v_{\text{mix}}^{\text{eff}}$ and $y_{ij}^{\text{eff}} = \rho v_{ij}^{\text{eff}}$.

For convex molecules $v_{ij}^{\text{eff}} = v_{ij}$ and $\alpha_{ij}^{\text{eff}} = \alpha_{ij}$, so that for a mixture containing only HCB molecules $v_{\text{mix}}^{\text{eff}} = v_{\text{mix}}$ and $\alpha_{\text{mix}}^{\text{eff}} = \alpha_{\text{mix}}$, and Eq. (26) is reduced to Eq. (25). Therefore, Eq. (26) applies to hard-body mixtures regardless of whether they have only convex molecules or not. However, we must take into account the fact that, when species i and j are both convex molecules, it holds that $v_{ij} = v_{ji}$ and $\alpha_{ij} = \alpha_{ji}$. By contrast, when one, or both, of the molecules is nonconvex $v_{ij}^{\text{eff}} \neq v_{ji}^{\text{eff}}$ and $\alpha_{ij}^{\text{eff}} \neq \alpha_{ji}^{\text{eff}}$, in general. This is because for nonconvex molecules, as Fig. 1 shows, the effective volume v_{ii}^{eff} corresponding to molecule i as “seen” by another molecule of the same species is not the same, in general, as the volume v_{ij}^{eff} of a molecule of species i as “seen” by a molecule of species j , which in turn is different from v_{ji}^{eff} , the volume of a molecule of species j as “seen” by a molecule of species i .

IV. DETERMINATION OF THE PARAMETERS

For a pure fluid consisting of linear homonuclear FHS molecules, the effective nonsphericity parameter α^{eff} can be defined [20] in the form

$$\alpha^{\text{eff}} = \frac{1}{3\pi} \frac{(\partial v^{\text{eff}} / \partial \sigma)(\partial^2 v^{\text{eff}} / \partial \sigma^2)}{v^{\text{eff}}}, \quad (30)$$

where σ is the diameter of one of the spheres that form the molecule and, for a FHS molecule consisting of n spheres with center to center distance l , the effective volume is given by [20]

$$v^{\text{eff}} = \frac{\pi \sigma^3}{6} \left[1 + 3L^* - \frac{L^{*3}}{2(n-1)^2} - 3(n-1)h^* \theta \right], \quad (31)$$

where $L^* = L/\sigma = (n-1)l^*$, $l^* = l/\sigma$, $h^* = h/\sigma = (1 - l^{*2}/4)^{1/2}$, and $\theta = \sin^{-1}(l^*/2)$, so that

$$\frac{\partial v^{\text{eff}}}{\partial \sigma} = \frac{\pi \sigma^2}{2} \left[1 + \frac{5L^*}{2} - 3(n-1)h^* \theta - \frac{L^{*2} \theta}{4(n-1)h^*} \right] \quad (32)$$

and

$$\begin{aligned} \frac{\partial^2 v^{\text{eff}}}{\partial \sigma^2} = \pi \sigma \left[1 + 2L^* - 3(n-1)h^* \theta - \frac{3L^{*2} \theta}{8(n-1)h^*} \right. \\ \left. + \frac{L^{*3}}{16(n-1)^2 h^{*2}} + \frac{L^{*4} \theta}{32(n-1)^3 h^{*3}} \right]. \quad (33) \end{aligned}$$

For the mixtures in which we are interested here, namely binary mixtures of linear fused hard spheres with hard spheres, expressions (30), (31), (32), and (33) with $n=2$ or 3 can be used to obtain v_{11}^{eff} and α_{11}^{eff} , that is, the parameters corresponding to the interaction of two identical FHS molecules. For the sphere-sphere interaction we will have $v_{22}^{\text{eff}} = v_{22} = (\pi/6)\sigma^3$ and $\alpha_{22}^{\text{eff}} = \alpha_{22} = 1$. These expressions also

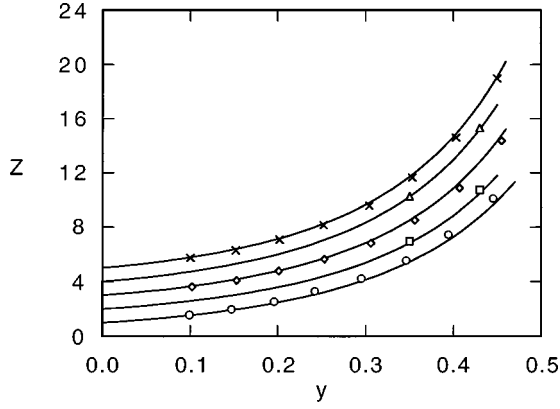


FIG. 4. Compressibility factor of HMD-HS mixtures for spheres with the same diameter as that of each of the spheres that form the dumbbell, as a function of the packing fraction y of the mixture. Points: simulation data from Refs. [21] and [22], for $x_1=0.1$ (circles), $x_1=0.25$ (squares), $x_1=0.5$ (diamonds), $x_1=0.75$ (triangles), and $x_1=0.9$ (crosses). Continuous line: Eqs. (26), (40), and (45), indistinguishable at the scale of the figure. For clarity, each curve, and the corresponding simulation data, have been displaced upwards a unit with respect to that immediately below.

apply for v_{21}^{eff} and α_{21}^{eff} , the volume of a sphere as ‘‘seen’’ by a FHS molecule and the corresponding nonsphericity parameter. For v_{12}^{eff} , the effective volume of a FHS molecule as ‘‘seen’’ by a sphere, expression (31) is no longer valid unless the diameter of the sphere is equal to the diameter of each of the spheres that form the dumbbell. For α_{12}^{eff} , definition (30) also needs to be modified, because now, in general, we have two different diameters.

To determine v_{12}^{eff} , consider Fig. 1(b). We will have

$$v_{12}^{\text{eff}} = \frac{\pi}{6} \sigma_1^3 \left[1 + \frac{3}{2} L^* (\sigma_2^{*2} + 1) - \frac{L^{*3}}{2(n-1)^2} - 3h^*(n-1)\theta\sigma_2^{*2} \right], \quad (34)$$

where now $h = [(\sigma_1 + \sigma_2)^2/4 - l^2/4]^{1/2}$, $\theta = \arcsin[l/(\sigma_1 + \sigma_2)]$, and an asterisk on a quantity means that it is in units of σ_1 .

Then, we can generalize definition (30) to the form

$$\alpha_{12}^{\text{eff}} = \frac{1}{3\pi} \frac{v'_{12}{}^{\text{eff}} v''_{12}{}^{\text{eff}}}{v_{12}^{\text{eff}}}, \quad (35)$$

where

$$v'_{12}{}^{\text{eff}} = \left(\frac{\partial v_{12}^{\text{eff}}}{\partial \sigma_1} \right) + \left(\frac{\partial v_{12}^{\text{eff}}}{\partial \sigma_2} \right) \quad (36)$$

and

$$v''_{12}{}^{\text{eff}} = \left(\frac{\partial^2 v_{12}^{\text{eff}}}{\partial \sigma_1^2} \right) + 2 \left(\frac{\partial^2 v_{12}^{\text{eff}}}{\partial \sigma_1 \partial \sigma_2} \right) + \left(\frac{\partial^2 v_{12}^{\text{eff}}}{\partial \sigma_2^2} \right). \quad (37)$$

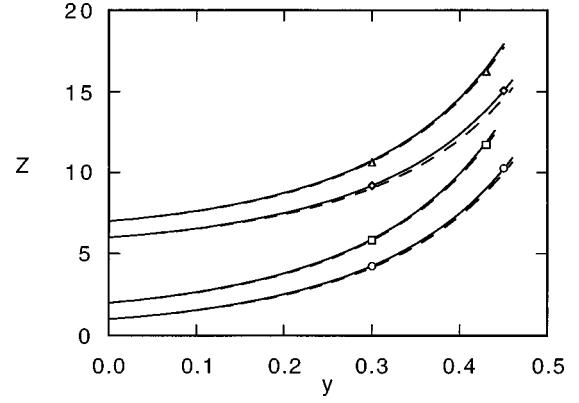


FIG. 5. As in Fig. 4 for spheres with volume v_2 equal to the volume v_1 of the dumbbells (the two lowest curves) and for spheres with $v_2 = \frac{3}{2}v_1$ (the two highest ones). In all cases $x_1=0.5$. Points: simulation data from Ref. [22] for $l^*=0.6$ (circles and diamonds), $l^*=1$ (squares and triangles). Continuous line: Eqs. (26) and (40), indistinguishable at the scale of the figure. Dashed line: Eq. (45). From top down, for clarity the first, second, and third curve, and the corresponding simulation data, have been displaced upwards six, five, and one unit, respectively.

These derivatives can be readily obtained from Eq. (34) in the form

$$v'_{12}{}^{\text{eff}} = \frac{\pi}{2} \sigma_1^2 \left[1 + \frac{L^*(2\sigma_2^{*2} + 2\sigma_2^* + 1)}{\sigma_2^* + 1} - 3h^*(n-1)\sigma_2^*\theta - \frac{L^2\sigma_2^*\theta}{4h^*(n-1)} - \frac{(\sigma_2^{*2} - 1)\sigma_2^*\theta}{4h^*(n-1)} \right], \quad (38)$$

and

$$v''_{12}{}^{\text{eff}} = \pi \sigma_1 \left\{ 1 + \left[1 + \frac{\sigma_2^*(3\sigma_2^* + 5)}{2(\sigma_2^* + 1)^2} \right] L^* + \frac{L^{*3}\sigma_2^*}{(\sigma_2^* + 1)8h^{*2}(n-1)^2} + \frac{L^*\sigma_2^*(\sigma_2^{*2} - 1)}{(\sigma_2^* + 1)8h^{*2}} - 3h^*(n-1)\theta - \frac{3L^{*2}}{8h^*(n-1)}\theta + \frac{L^{*4}}{32h^{*3}(n-1)^3}\theta - \frac{(-3\sigma_2^{*2} + 2\sigma_2^* + 1)L^{*2}\theta}{32h^{*3}(n-1)} - \frac{(\sigma_2^{*2} - 1)\theta}{2h^*(n-1)} \right\}. \quad (39)$$

It can be seen that, for $\sigma_1 = \sigma_2 = \sigma$, expressions (34), (38), and (39) reduce to Eqs. (31), (32), and (33), respectively.

V. RESULTS AND DISCUSSION

From the expressions derived in the preceding section, together with Eqs. (28) and (29), we have determined the values of the parameters for the types of mixtures considered in this paper. They are listed in Table I.

According to the considerations of Sec. III, the ratio $[Z_{\text{mix}}^{\text{HB}} - 1]/[Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}}^{\text{eff}}) - 1]$ should be a constant for any density. In order to test whether this is the case, we have plotted this ratio in Fig. 2 for several different mixtures of hard

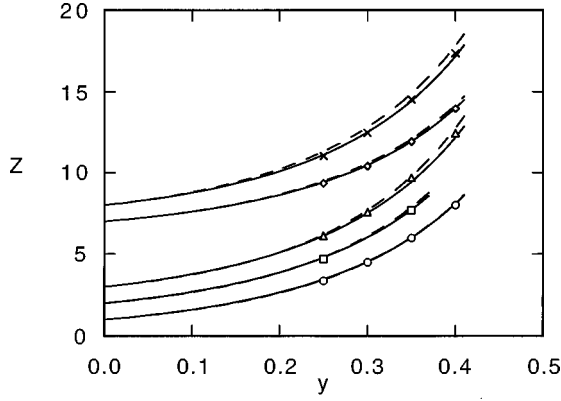


FIG. 6. As in Fig. 4 for HMLST-HS mixtures. The three lowest curves correspond to spheres with the same diameter as that of each sphere that forms the triatomic molecule, and the two highest curves correspond to spheres with volume v_2 equal to the volume v_1 of the triatomic molecules. In every case $l^* = 0.8$. Points: simulation data from Refs. [23, 24]. For the four highest curves, the continuous line represents the results from Eq. (45), and the dashed line represents those from Eqs. (40) and (45), indistinguishable at the scale of the figure. The three equations are indistinguishable in the lowest curve at the scale of the figure. Dashed line: Eq. (45). From top down, for clarity, the first, second, third, and fourth curves, and the corresponding simulation data, have been displaced upwards seven, six, two, and one unit, respectively.

TABLE I. Parameters involved in equation of state (23) for the mixtures considered. Lengths are in units of σ_1 , and volumes in units of σ_1^3 . v_{mix} is the mean volume of a molecule in the mixture. In every case, subscript 2 refers to the spheres.

x_1	v_{mix}	$v_{\text{mix}}^{\text{eff}}$	$\alpha_{\text{mix}}^{\text{eff}}$
HS+HMD			
$l_1 = 1/\sigma_1 = \sigma_2$			
0.10	0.5760	0.5833	1.0605
0.25	0.6545	0.6728	1.1379
0.50	0.7854	0.8219	1.2446
0.75	0.9163	0.9711	1.3344
0.90	0.9948	1.0606	1.3831
$l_1 = 0.6/\sigma_1 = \sigma_2$			
0.50	0.7309	0.7383	1.0717
$l_1 = 1/v_1 = v_2$			
0.50	1.0472	1.0876	1.2055
$l_1 = 0.6/v_1 = v_2$			
0.50	0.9383	0.9463	1.0711
$l_1 = 1/v_1 = (2/3)v_2$			
0.50	1.1729	1.1814	1.0633
$l_1 = 0.6/v_1 = (2/3)v_2$			
0.50	1.3090	1.3518	1.1811
HS+HMLST			
$l_1 = 0.8/\sigma_1 = \sigma_2$			
0.25	0.7732	0.7887	1.2079
0.50	1.0229	1.0538	1.3460
0.75	1.2726	1.3188	1.4564
$l_1 = 0.8/v_1 = v_2$			
0.25	1.5222	1.5423	1.1362
0.75	1.5222	1.5732	1.4118

spheres with homonuclear hard dumbbells (HMD) and in Fig. 3 for mixtures of hard spheres with hard homonuclear linear symmetric triatomics (HMLST). For $Z_{\text{mix}}^{\text{HB}}$ we have used the simulation data [21–24], and for $Z_{\text{mix}}^{\text{HS}}$ Eq. (21). Although in several cases the simulation data are scarce, it can be seen that the constancy holds very accurately.

On the other hand, according to Eq. (26) the value of the above-mentioned ratio must be very approximately $\alpha_{\text{mix}}^{\text{eff}}$. In the same figures we have plotted the values of this parameter showing that they are consistent with the value of the ratio.

In Figures 4–6 the results from equation of state (26) are compared with those from the equation of state

$$Z^{\text{SPT}} = \frac{1}{(1-y)} + \frac{3\alpha y}{(1-y)^2} + \frac{y^2[(49\alpha - 31) - y(11\alpha - 7) - y^2(25\alpha - 21)]}{6(1-y)^3}, \quad (40)$$

where y is the packing fraction of the mixture and

$$\alpha = \frac{\sum_i x_i R_i \sum_i x_i S_i}{3 \sum_i x_i v_i} \quad (41)$$

is the nonsphericity parameter of the mixture. For homonuclear FHS with diameter σ and reduced center to center distance $l^* = l/\sigma > 0.5$, parameters R , S , and v are given by

$$R = [(m-1)l^* + 2]\sigma/4, \quad (42)$$

$$S = [(m-1)l^* + 1]\pi\sigma^2, \quad (43)$$

and

$$v = [\frac{1}{2}(m-1)(3l^* - l^{*3}) + 1]\pi\sigma^3/6. \quad (44)$$

Equation (40) was derived [25] on the basis of the form of the SPT equation of state, and proved [26] to be very accurate for the kind of mixtures we are considering here.

The same figures also include the results from BHS theory, which expresses the equation of state for a multicomponent mixture of polyatomic molecules in the form [11]

$$Z_{\text{mix}}^{\text{BHS}} = \frac{PV}{N_m kT} = \sum_i x_m(i) N_s(i) Z_{\text{mix}}^{\text{HS}} - \sum_i x_m(i) \times \sum_{\text{bonds}} \left[1 + \frac{\rho}{g_{jk}^{\text{HS}}(\sigma_{jk})} \left(\frac{\partial g_{jk}^{\text{HS}}(\sigma_{jk})}{\partial \rho} \right)_{T,N} \right], \quad (45)$$

where N_m is the total number of molecules and $x_m(i)$ is the mole fraction of molecules of species i , each of them formed by $N_s(i)$ hard spheres. The sum over bonds is taken over the number of bonding contacts jk between the spheres j and k of a molecule of species i , and $g_{jk}^{\text{HS}}(\sigma_{jk})$ is obtained from Eq. (21). Although, in principle, BHS theory applies to fluids

consisting of molecules formed by nonoverlapping spheres, it can also be used for FHS fluids [11]. To do so, the FHS molecule is replaced by an equivalent BHS, in which the relative diameters of the spheres are chosen in such a way that the relation $\alpha_{\text{FHS}} = \alpha_{\text{BHS}}$ is satisfied. The nonsphericity parameter is determined from Eq. (4) using expressions of R , S , and v derived for diatomic [27] and triatomic [28] molecules.

As can be seen in Figs. 4 and 5, for HS-HMD mixtures, Eq. (26) and the SPT Eq. (40) give nearly the same accuracy in all cases. The BHS results from Eq. (45) agree with those from the two preceding equations for mixtures in which HMD molecules consist of tangent spheres, but its accuracy worsens when the spheres of the diatomic molecule overlap.

With regard to the results for HS-HMLST mixtures, Fig. 6 shows that there is excellent agreement between Eq. (26) and simulation in all cases. The accuracy of SPT and BHS results is very good for mixtures with low values of the mole fraction of HMLST, but worsens slightly as the concentration of HMLST molecules increases.

To summarize, in this paper we have extended an equation of state previously developed for HCB fluid mixtures to mixtures in which at least one of the components consists of nonconvex molecules. The parameters involved in the equation of state can be determined from the geometry of the molecules forming the mixture. To do so, expressions for determining these parameters have been obtained. The results are in close agreement with simulation data for HS-

HMD and HS-HMLST mixtures and compare favorably with those from SPT and BHS theories.

The derived equation of state is intended for use in the normal fluid density range. It should be interesting to test its performance for higher densities but, to the best of our knowledge, simulation data are not available in that range for the mixtures considered here. Moreover, we must be careful in applying this equation of state to higher densities, because evidence has been found [29,30] of demixing phase transitions in different binary hard-core mixtures at high densities. Additionally, binary mixtures of prolate and oblate molecules can exhibit a variety of phases at high densities [30], before demixing occurs.

On the other hand, it has been shown [31] that the equation of state (21) for hard sphere mixtures, in which is based the equation of state derived here, is inaccurate at densities close to the solid-fluid transition for large size ratios. Theoretical evidence has been provided [32] about the possible existence of a demixing phase transition in additive hard sphere mixtures, which could explain this inaccuracy. Therefore, it seems likely that our equation will also fail at densities higher than those corresponding to the normal fluid.

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