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Equation of state for fluid mixtures of hard spheres and heteronuclear hard dumbbells

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A theoretically founded equation of state is developed for mixtures of hard spheres with heteronuclear hard dumbbells. It is based on a model previously developed for hard-convex-body fluid mixtures, and further extended to fluid mixtures of homonuclear hard dumbbells. The equation scales the excess compressibility factor for an equivalent hard-sphere fluid mixture to obtain that corresponding to the true mixture. The equivalent mixture is one in which the averaged volume of a sphere is the same as the effective molecular volume of a molecule in the real mixture. Thus, the theory requires two parameters, namely the averaged effective molecular volume of the molecules in the mixture and the scaling factor, which is the effective nonsphericity parameter. Expressions to determine these parameters are derived in terms of the geometrical characteristics of the molecules that form the mixture. The overall results are in closer agreement with simulation data than those obtained with other theories developed for these kinds of mixtures. © 1999 American Institute of Physics. [S0021-9606(99)51134-3]

I. INTRODUCTION

Perturbation theories are among the most fruitful approaches for dealing with thermodynamic properties of fluids whose molecules interact through realistic intermolecular forces. The basis of such theories is the fact that fluid properties are mainly determined by the repulsive interactions between the molecules, whereas attractive interactions are relatively of minor importance and their contribution can be treated as a perturbation of the repulsive contribution. This leads to the expression of the thermodynamic properties in terms of a power series expansion of a parameter characterizing the strength of the attractive forces. In general, only the first three terms of this expansion are needed to obtain satisfactory results. The zero-order term corresponds to the lack of attractive forces or, equivalently, to the infinite temperature limit. This defines a reference system, from whose properties the next two perturbation terms can be obtained. Therefore, in perturbation theories it is of crucial importance to know the thermodynamic properties of the reference system with sufficient accuracy. It seems clear that the most suitable reference system should be one consisting of hard molecules with the same shape as the real molecules and a temperature-dependent volume.

This is one of the reasons for the long-lived interest in the study of the thermodynamic properties of hard-body (HB) fluids. Another reason is that they are more appropriate to start with in the development of a theory of fluids, because of their greater simplicity as compared with real fluids and the relative abundance of simulation data for a variety of molecular shapes.

Similar considerations apply to mixtures and, thus, a number of theories for the thermodynamic properties of HB

fluid mixtures have been derived from theories previously developed for pure HB fluids. Of particular interest for the fluids considered in this paper are scaled particle theory (SPT) and bonded-hard-sphere (BHS) theory. Our interest in the former is for two reasons. On the one hand, SPT for hard sphere (HS) fluid mixtures¹ provided the basis for developing² an accurate equation of state for these mixtures. The same result was obtained independently³ starting from the Percus–Yevick (PY) theory for HS mixtures.⁴ This equation is used here as the equation of state for the equivalent HS mixture. On the other hand, starting from the SPT derived for hard convex body (HCB) fluid mixtures,⁵ several improved equations of state have been obtained^{6–10} and widely used for both convex and nonconvex HB fluid mixtures.

In a recent paper,¹¹ an accurate equation of state was developed for pure fluids consisting of heteronuclear hard dumbbells (HTDs). This was based on an equation of state previously derived¹² for pure HCB fluids and later extended¹³ to homonuclear fused hard sphere (FHS) pure fluids. The theory required two parameters which were determined from the molecular geometry.

Very recently,¹⁴ a theoretically based equation of state for HCB fluid mixtures has been derived and further extended¹⁵ to fluid mixtures of FHS with hard spheres. Although similar in form to the equation of state for pure fluids, the equation of state for HCB fluid mixtures cannot be obtained by simply introducing suitable mixing rules. Knowledge of the parameters for the pure fluids which form the mixture does not allow us to determine the parameters of the mixture. This is a nontrivial task for the mixtures we are considering here.

The aim of this paper is twofold: first, to test the performance of the theory for binary fluid mixtures of hard heteronuclear diatomic molecules with hard spheres and, second, to

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obtain analytical expressions to determine the parameters for these mixtures.

Section II summarizes the derivation of the equation of state for pure HB fluids. The theory for HB fluid mixtures is derived in Sec. III in some detail. In Sec. IV the results are compared with simulation data and with those from other theories. Finally, expressions to determine the parameters are derived in the Appendix.

II. EQUATION OF STATE FOR PURE HARD BODY FLUIDS

For a pure fluid consisting of hard spheres of diameter σ , the virial theorem allows us to express the compressibility factor in the form

$$Z^{\text{HS}} = \frac{PV}{NkT} = 1 + \frac{1}{6} \rho S_{1+2} \sigma g^{\text{HS}}(0) = 1 + \frac{2}{3} \pi \rho \sigma^3 g^{\text{HS}}(0), \quad (1)$$

where $\rho = N/V$ is the number density, $g^{\text{HS}}(0)$ is the pair correlation function at contact distance, and $S_{1+2} = 2S + 8\pi R^2 = 4\pi\sigma^2$ is the surface defined by the center of sphere 2 moving around sphere 1 while the two remain in contact, that is, at center to center distance $\sigma = 2R$.

Analogously, for a pure HCB fluid, we can define $g^{\text{av}}(0)$, the contact value of the averaged pair correlation function, weighted over surface area, and $\sigma^{\text{av}} = \langle \mathbf{r}_{12} \cdot \nu \rangle$, the average of the vector distance \mathbf{r}_{12} between the centers of the two molecules projected over ν , the unit vector normal to the surface at the contact point, with both averages taken over all possible orientations of the pair of molecules. Then, the compressibility factor can be expressed in the form¹⁶

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

In this expression $S_{1+2} = 2S + 8\pi R^2$ has the same meaning as for hard spheres, except for the fact that now it is a quantity averaged over orientations and R is the $(1/4\pi)$ multiple of the mean curvature integral, whose expression depends on the shape of the molecules.

Consider now a HS fluid in which the spheres have a molecular volume $v_m = (\pi/6)\sigma^3$ equal to that of the HCB molecules, with both kinds of fluid at the same density ρ . From Eqs. (1) and (2), the ratio of the excess compressibility factor for the two fluids can be expressed in the form

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

where we have introduced the nonsphericity parameter, or shape factor α , defined as

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

It has been shown¹⁷ that the structure of a HS fluid mimics rather well that of a hard ellipsoid fluid in the contact region when both fluids have the same number density and the same molecular volume. On the other hand, evidence has been found¹⁸ that the atom-atom pair correlation function of diatomic liquids can be accurately modeled by that of an

atomic liquid in the same corresponding state by properly scaling the radial distances in the latter. A similar scaling of the pair correlation function was used before in the Parson's¹⁹ "decoupling approximation" to map a system of hard rods into a system of hard spheres. The same approximation has been used more recently²⁰ for more complex molecular models.

Therefore, it seems reasonable to expect that, at contact distance, the averaged pair correlation function of the HCB fluid could be obtained from that of the HS fluid by means of some sort of scaling. This is indeed the case. Simulation data on $g^{\text{av}}(0)$ and σ^{av} existing for some HCB fluids at moderate to high densities led¹² to the scaling law

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

When this is introduced in Eq. (3), the right-hand side depends only on molecular shape and therefore the ratio $(Z^{\text{HCB}} - 1)/(Z^{\text{HS}} - 1)$ should be a constant for a given fluid, whatever the density. This constancy was found¹² to hold for HCB fluids of any shape, except perhaps for very large values of α , when the ratio, Eq. (3), is calculated from simulation data for Z^{HCB} and the Carnahan-Starling²¹ equation

$$Z^{\text{CS}} = \frac{1 + y + y^2 - y^3}{(1 - y)^3}, \quad (6)$$

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

Furthermore, the small error introduced in Eq. (3) by the approximation involved in the scaling law, Eq. (5), is almost offset by introducing the additional approximation

$$\frac{1}{2} \left(\alpha + \frac{\frac{4}{3}\pi R^3}{v_m} \right) \approx \alpha, \quad (7)$$

which is exact for hard spheres and holds well for HCB fluids with values of α that are not too large. Then, the final form of the equation of state is

$$Z^{\text{HCB}} = 1 + \alpha(Z^{\text{CS}} - 1), \quad (8)$$

where α can be determined from Eq. (4) using standard formulas²² for R , S , and v_m . This proved¹² to be very accurate for all HCB fluids except perhaps for those with extreme values of the shape factor α .

The equation of state (8) was extended^{11,13} to FHS fluids by introducing the effective parameters v_m^{ef} and α_{ef} , instead of v_m and α . This must be done to account for the fact that a nonconvex molecule excludes any point of another molecule from a volume greater than the molecular volume. Thus, we must consider the fluid at density ρ as having an effective packing fraction $y_{\text{ef}} = \rho v_m^{\text{ef}}$ instead of y . Then, the equation of state becomes¹³

$$Z^{\text{FHS}} = 1 + \alpha_{\text{ef}}[Z^{\text{CS}}(y_{\text{ef}}) - 1]. \quad (9)$$

The effective nonsphericity parameter α_{ef} for nonconvex hard bodies cannot be determined from expression (4) because the radius of curvature is not well defined. For linear homonuclear FHS molecules, an alternative definition has been proposed²³

$$\alpha_{\text{ef}} = \frac{1}{3\pi} \frac{(\partial v_m^{\text{ef}} / \partial \sigma)(\partial^2 v_m^{\text{ef}} / \partial \sigma^2)}{v_m}. \quad (10)$$

Expressions for v_m^{ef} and α_{ef} have been derived²³ from this definition for linear homonuclear FHS fluids.

For heteronuclear FHS fluids, a generalization of definition [Eq. (10)] has been proposed,¹¹ as well as suitable expressions for v_m^{ef} .

With the effective parameters determined in these ways, Eq. (9) showed very good agreement, with simulation data, for both homonuclear¹³ and heteronuclear¹¹ FHS fluids. Equation (9) applies also to convex molecules, provided that we take into account that, in this case, $y_{\text{ef}} = y$ and $\alpha_{\text{ef}} = \alpha$, where α is given by Eq. (4). However, for very anisotropic molecules, that is for molecules having relatively high values of α , the ratio $(Z^{\text{HB}} - 1) / [Z^{\text{CS}}(y_{\text{ef}}) - 1]$ is no longer a constant, but a function varying more or less smoothly with density. The equation of state is then¹¹

$$Z^{\text{HB}} = 1 + B_2^*(y_{\text{ef}})y_{\text{ef}} + 4\alpha_{\text{ef}}y_{\text{ef}} \left[\frac{Z^{\text{CS}}(y_{\text{ef}}) - 1}{4y_{\text{ef}}} - 1 \right], \quad (11)$$

where $B_2^*(y_{\text{ef}}) = B_2^*(y)v_m/v_m^{\text{ef}}$. For fluids with low to moderate values of α , the difference between Eqs. (9) and (11) is small and, within the statistical uncertainty of the simulation data, Eq. (9) holds in most cases.

III. EQUATION OF STATE FOR HARD BODY FLUID MIXTURES

We will start by deriving the equation of state for HCB fluid mixtures and then we will generalize it to mixtures including nonconvex molecules, as was done in Sec. II for pure fluids. The generalization of Eq. (2) to HCB fluid mixtures is expressed in the form

$$Z_{\text{mix}}^{\text{HCB}} = 1 + \frac{1}{6} \sum_{i,j} \rho x_i x_j S_{i+j} \sigma_{ij}^{\text{av}} g_{ij}^{\text{av}}(0), \quad (12)$$

where x_i and x_j are the mole fractions of components i and j in the mixture. As a particular case, this expression applies to HS mixtures. For this case, the equation of state is accurately given by

$$Z_{\text{mix}}^{\text{HS}} = \frac{6}{\pi\rho} \left(\frac{\zeta_0}{1-\zeta_3} + \frac{3\zeta_1\zeta_2}{(1-\zeta_3)^2} + \frac{3\zeta_2^3}{(1-\zeta_3)^3} - \frac{\zeta_3\zeta_2^3}{(1-\zeta_3)^3} \right), \quad (13)$$

with

$$\zeta_l = \frac{\pi\rho}{6} \sum_i x_i (\sigma_i)^l, \quad (14)$$

where σ_i is the diameter of spheres of component i . The ζ_l are related to the packing fraction y_{mix} of the mixture through $\rho = y_{\text{mix}}/v_{\text{mix}}$, where

$$v_{\text{mix}} = \sum_{i,j} x_i x_j v_{ij}, \quad (15)$$

with

$$v_{ij} = (v_{ii} + v_{jj})/2. \quad (16)$$

Equation (13) has been derived independently by two different routes. One of them³ starts from the compressibility and virial solutions⁴ of the PY integral equation for mixtures. The two solutions are combined with a weighting of 2/3 and 1/3, respectively, similarly to the way in which the CS equation (6) for a pure HS fluid can be derived from solutions of the PY theory^{24,25} for pure fluids. The other procedure² uses the fact that the CS equation can be obtained from a modification of the SPT equation²⁶ for a pure hard spheres fluid. The same modification is applied to the SPT equation for HS mixtures¹ to derive Eq. (13). In any case, we can say that when several pure HS fluids which obey the CS equation of state are mixed together, the resulting HS mixture will obey Eq. (13).

Let us consider now each of the pure fluids which form the HCB mixture. Applying the procedure outlined in the previous section, from Eq. (8) we will arrive at

$$\frac{Z_{ii} - 1}{\alpha_{ii}} = Z^{\text{CS}}(y_{ii}) - 1. \quad (17)$$

According to this expression, the excess compressibility factor of a pure HCB fluid, when scaled by means of its non-sphericity parameter, reduces to that of a pure HS fluid whose spheres have the same molecular volume as the HCB molecules. If all these “scaled” fluids are mixed together, a HS fluid mixture will result. Therefore, by introducing a suitable scaling parameter α_{mix} for the mixture, we will have

$$\frac{Z_{\text{mix}}^{\text{HCB}} - 1}{\alpha_{\text{mix}}} = Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}}) - 1. \quad (18)$$

Here, $Z_{\text{mix}}^{\text{HS}}$ is the compressibility factor of a mixture of hard spheres with an averaged molecular volume v_{mix} given by Eq. (15), which is equal to that corresponding to the HCB mixture because we are considering that 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, since we are considering that pure HS fluids obey the CS equation (6), the HS mixture must obey Eq. (13), as stated before. Using this equation and simulation data for $Z_{\text{mix}}^{\text{HCB}}$, we have shown¹⁴ that the ratio $[Z_{\text{mix}}^{\text{HCB}} - 1] / [Z_{\text{mix}}^{\text{HS}} - 1]$ is essentially independent of density. This implies that α_{mix} is a purely geometrical parameter; that is, the density dependence of the excess compressibility factor of HCB and HS mixtures is the same. This allows us to determine the scaling parameter of the mixture in a simple way. To do so, suppose that the procedure followed in Sec. II to derive the equation of state of the HCB pure fluid, is applicable to each of the terms in the sum Eq. (12). That will result in

$$Z_{\text{mix}}^{\text{HCB}} = 1 + \sum_{i,j} \alpha_{ij} [Z^{\text{CS}}(y_{ij}) - 1]. \quad (19)$$

The first order term in the low density expansion of this expression is

$$Z_{\text{mix}}^{\text{HCB}} - 1 \approx \sum_{i,j} \alpha_{ij} 4y_{ij} = \sum_{i,j} \alpha_{ij} \frac{v_{ij}}{v_{\text{mix}}} 4y_{ij} \frac{v_{\text{mix}}}{v_{ij}} \\ = 4y_{\text{mix}} \sum_{i,j} \alpha_{ij} x_i x_j \frac{v_{ij}}{v_{\text{mix}}}. \quad (20)$$

Since for a pure HS fluid $\alpha = 1$, if we apply Eq. (19) to a HS mixture, taking $\alpha_{ij} = 1$ for every i and j , we obtain

$$Z_{\text{mix}}^{\text{HS}} = 1 + \sum_{i,j} [Z^{\text{CS}}(y_{ij}) - 1], \quad (21)$$

and, at low densities

$$Z_{\text{mix}}^{\text{HS}} - 1 \approx 4y_{\text{mix}} \sum_{i,j} x_i x_j \frac{v_{ij}}{v_{\text{mix}}} = 4y_{\text{mix}}. \quad (22)$$

To arrive at the last equality we have taken into account Eq. (15). Introducing the preceding result into Eq. (18) we have

$$Z_{\text{mix}}^{\text{HCB}} - 1 \approx \alpha_{\text{mix}} 4y_{\text{mix}}, \quad (23)$$

By comparing results of Eqs. (20) and (23) we obtain the expression of α_{ef} we are looking for

$$\alpha_{\text{mix}} = \sum_{i,j} x_i x_j \alpha_{ij} \frac{v_{ij}}{v_{\text{mix}}}. \quad (24)$$

According to this expression, the scaling parameter α_{mix} depends on the shape of the molecules that forms the mixture but not on density. Therefore, although it has been derived from a low density expansion, it should hold at any density. This is in agreement with our previous statement that the ratio $[Z_{\text{mix}}^{\text{HCB}} - 1]/[Z_{\text{mix}}^{\text{HS}} - 1]$ does not depend on density.

It should be noted that neither Eq. (21) nor Eq. (19) have the correct forms of Eqs. (13) and (18), respectively. The fact is that the former two scale at low densities much in the same way as do the latter two at any density. This, which will be confirmed in Sec. IV, provides an easy way to determine the parameter α_{mix} to be used in the right equation which can be expressed in the form

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

in which the parameters α_{mix} and v_{mix} are given by Eqs. (15) and (24), respectively, and $Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}})$ by Eq. (13). According to our criterion, in a mixture of spheres of different sizes, $\alpha_{ij} = 1$ for every i and j , and then Eq. (25) is reduced to the equation of state (13) for the hard-sphere fluid mixture.

Equation (24) must not be interpreted as a mixing rule because it is not used in combination with the pure fluid equation of state to obtain the equation of state of the mixture. This parameter scales the excess compressibility factor of an *equivalent hard sphere mixture* to obtain that for the HCB mixture. The equivalent mixture is one with the same number of species as the HCB mixture and such that the molecular volume is the same for a species in the HCB mixture and for its counterpart in the equivalent mixture. In fact, parameter α_{mix} is not even exactly a nonsphericity parameter for the mixture. As stated before, for an HS fluid mixture Eq. (24) gives $\alpha_{\text{mix}} = 1$, whereas from the exact value of the second virial coefficient

$$B_{\text{mix}}^{\text{HS}} = \frac{\sum_{i,j} x_i x_j v_{ij} + 3 \sum_{i,j} x_i x_j v_i^{1/3} v_j^{2/3}}{\sum_{i,j} x_i x_j v_{ij}}, \quad (26)$$

we can obtain a nonsphericity parameter $\alpha_{\text{mix}}^{\text{HS}}$ if we put $B_{\text{mix}}^{\text{HS}} = 1 + 3\alpha_{\text{mix}}^{\text{HS}}$ as for pure HCB fluids. This gives

$$\alpha_{\text{mix}}^{\text{HS}} = \frac{\sum_{i,j} x_i x_j v_i^{1/3} v_j^{2/3}}{\sum_{i,j} x_i x_j v_{ij}}, \quad (27)$$

which in general differs from unity, unlike the result from Eq. (24).

Equation (25) provides¹⁴ very good agreement with simulation data for binary HCB fluid mixtures. Its extension to FHS fluid mixtures is straightforward. In a similar way to what was done for pure fluids in Sec. II, we only need to replace the parameters v_{mix} and α_{mix} with the effective ones $v_{\text{mix}}^{\text{ef}}$ and $\alpha_{\text{mix}}^{\text{ef}}$. As a consequence, an effective packing fraction $y_{\text{mix}}^{\text{ef}} = \rho v_{\text{mix}}^{\text{ef}}$ must also be introduced instead of the packing fraction y . The resulting equation of state is

$$Z_{\text{mix}}^{\text{HB}} = 1 + \alpha_{\text{mix}}^{\text{ef}} [Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}}^{\text{ef}}) - 1], \quad (28)$$

where

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

and

$$\alpha_{\text{mix}}^{\text{ef}} = \sum_{i,j} x_i x_j \alpha_{ij}^{\text{ef}} \frac{v_{ij}^{\text{ef}}}{v_{\text{mix}}^{\text{ef}}}, \quad (30)$$

with

$$v_{\text{mix}}^{\text{ef}} = \sum_{i,j} x_i x_j v_{ij}^{\text{ef}}, \quad (31)$$

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

Equation (28) is a general equation of state for HB fluid mixtures in that it can be applied to FHS fluid mixtures as well as to HCB mixtures and to mixtures of convex with nonconvex molecules. This is so because for a mixture consisting only of convex molecules it holds that $v_{ij}^{\text{ef}} = v_{ij}$ and $\alpha_{ij}^{\text{ef}} = \alpha_{ij}$, so that $v_{\text{mix}}^{\text{ef}} = v_{\text{mix}}$ and $\alpha_{\text{mix}}^{\text{ef}} = \alpha_{\text{mix}}$, and Eq. (28) is reduced to Eq. (25).

There is another difference in the application of Eq. (28) to mixtures containing nonconvex molecules with respect to the case of mixtures consisting only of convex molecules. In the latter case, $v_{ij} = v_{ii}$, because the volume of a molecule of species i as “seen” by another molecule j is independent of whether the second molecule is of the same species as the first or not. For the same reason $v_{ji} = v_{jj}$, so that $v_{ij} + v_{ji} = v_{ii} + v_{jj}$ and we can average the volume for the interaction ij taking $v_{ij} = v_{ji} = (v_{ii} + v_{jj})/2$ as was done in Eq. (16). Similar considerations apply to α_{ij} . The situation is different when one, or both, of the molecules is nonconvex because $v_{ij}^{\text{ef}} \neq v_{ii}^{\text{ef}}$ and $v_{ji}^{\text{ef}} \neq v_{jj}^{\text{ef}}$ in general, as illustrated in Fig. 1. Therefore we must determine both v_{ij}^{ef} and v_{ji}^{ef} , as well as α_{ij}^{ef} and α_{ji}^{ef} in addition to v_{ii}^{ef} and α_{ii}^{ef} . That is, knowledge of the parameters corresponding to the pure fluids which form the mixture is not enough to determine the parameters of the mixture.

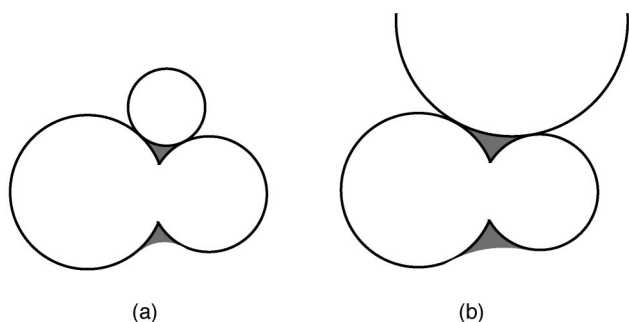


FIG. 1. Shaded area represents the difference between effective and real molecular volume of a heteronuclear dumbbell (a) as seen by a small sphere and (b) as seen by a big sphere.

These considerations also affect the way Eq. (13) must be applied. As stated before, for nonconvex molecules the effective volume of a given molecule i does not depend only on its geometry, but also on the geometry of the molecule j which interacts with i . The equivalent spheres must reflect this fact through their diameters or, equivalently, through Eq. (14). Therefore, we redefine the ζ_i in the form

$$\zeta_i = \frac{\pi \rho}{6} \sum_{ij} x_i x_j \sigma_{ij}^l, \quad (32)$$

where the diameter σ_{ij} for interaction ij is determined from $\sigma_{ij} = [(6/\pi) V_{ij}^{\text{eff}}]^{1/3}$, so that, in general $\sigma_{ij} \neq \sigma_{ji}$. For a hard sphere mixture, Eqs. (32) and (14) are equivalent. For a given mixture, when Eq. (32) is introduced into Eq. (13), the resulting equation of state can be expressed in terms of the effective packing fraction solely, where the notation $Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}}^{\text{eff}})$ is employed in Eq. (28).

IV. RESULTS AND DISCUSSION

In order to apply Eq. (28) to the mixtures considered in this paper, namely binary mixtures of heteronuclear hard dumbbells (species 1) with hard spheres (species 2) we have to determine the involved parameters $v_{\text{mix}}^{\text{eff}}$ and $\alpha_{\text{mix}}^{\text{eff}}$. Expressions to determine effective molecular volumes of HTD in a monocomponent fluid have been obtained previously¹¹ and used to determine the corresponding effective nonsphericity parameter from a generalization of definition, Eq. (10). They are useful here to determine the contributions v_{11}^{eff} and α_{11}^{eff} in Eqs. (31) and (30), respectively, for the dumbbells in the binary mixture. The contributions v_{22}^{eff} and α_{22}^{eff} , corresponding to the spheres, or v_{21}^{eff} and α_{21}^{eff} , corresponding to spheres as “seen” by a dumbbell are trivially determined as $v_{22}^{\text{eff}} = v_{22} = v_{22} = \pi \sigma_2^3/6$ and $\alpha_{22}^{\text{eff}} = \alpha_{12}^{\text{eff}} = \alpha_{22} = 1$. Therefore, we only need to determine the terms v_{12}^{eff} and α_{12}^{eff} , which correspond to the effective volume and nonsphericity parameter of a hard dumbbell as seen by a hard sphere. Expressions to do so are derived in the Appendix, and the values of the parameters for the mixtures of interest are listed in Table I.

In order to test the performance of equation of state (28), we will start by analyzing the constancy of the ratio $[Z_{\text{mix}}^{\text{HB}} - 1]/[Z_{\text{mix}}^{\text{HS}}(y_{\text{mix}}^{\text{eff}}) - 1]$ for any density, which is implicit in Eq. (28). This ratio is plotted in Fig. 2, taking for $Z_{\text{mix}}^{\text{HB}}$ the simulation data^{22,27} for several different mixtures, as a func-

TABLE I. Parameters involved in equation of state, Eq. (28), for the mixtures considered. σ_{1a} and l are, respectively, the diameter of the smallest sphere of the dumbbell and the center to center distance. σ_2 is the diameter of the single spheres. v_{mix} is the true average molecular volume in the mixture. All lengths are in units of σ_{1A} , the diameter of the biggest sphere of the dumbbell, and volumes are in units of σ_{1A}^3 .

x_1	v_{mix}	v_{11}^{eff}	v_{12}^{eff}	$v_{\text{mix}}^{\text{eff}}$	$\alpha_{\text{mix}}^{\text{eff}}$
$\sigma_{1a} = 0.5/\sigma_2 = l/l = 0.625$					
0.25	0.5381	0.5962	0.5973	0.5420	1.0394
0.50	0.5526	0.5962	0.5973	0.5602	1.0767
0.75	0.5671	0.5962	0.5973	0.5783	1.1119
$\sigma_{1a} = 0.5/\sigma_2 = 0.5/l = 0.625$					
0.25	0.1945	0.5962	0.5899	0.1970	1.1148
0.50	0.3235	0.5962	0.5899	0.3293	1.1354
0.75	0.4526	0.5962	0.5899	0.4623	1.1426
$v_1 = v_2/l = 0.625$					
0.25	0.5816	0.5962	0.5977	0.5855	1.0364
0.50	0.5816	0.5962	0.5977	0.5893	1.0727
0.75	0.5816	0.5962	0.5977	0.5928	1.1090

tion of the effective packing fraction $y_{\text{mix}}^{\text{eff}}$ of the mixture. It can be seen that the constancy holds very accurately. Moreover, there is good agreement, within the statistical uncertainty of the simulation data, between the value of the constant and the value $\alpha_{\text{mix}}^{\text{eff}}$, as determined from Eq. (30), which according to Eq. (28) corresponds to the ratio.

Several of the most widely used equations of state for HB fluid mixtures were derived^{6–10} in one way or another from scaled particle theory. Among them, one of the most accurate for the mixtures considered here is expressed in the form^{9,10}

$$Z^{\text{SPT}} = \frac{1}{(1-y)} + \frac{3\alpha y}{(1-y)^2} + \frac{y^2[(49\alpha-31)-y(11\alpha-7)-y^2(25\alpha-21)]}{6(1-y)^3}. \quad (33)$$

In this equation y is the packing fraction of the mixture and α is the corresponding nonsphericity parameter, given by

$$\alpha = \frac{\sum_i x_i R_i \sum_i x_i S_i}{3 \sum_i x_i V_i}. \quad (34)$$

For FHS molecules, the nonsphericity parameter is determined from Eq. (24) taking the true molecular volume and surface, whereas R is determined as that corresponding to the enveloping convex body. For HTD consisting of spheres of diameters σ_a and σ_b and center to center distance $l = a + b$, where a and b are the distances from the centers of spheres to the intersecting plane, the corresponding expressions are¹⁰

$$R = [\sigma_a + \sigma_b + l + (\sigma_a - \sigma_b)^2/4l]/4, \quad (35)$$

$$S = \pi[\sigma_a^2 + \sigma_b^2 + 2\sigma_a a + 2\sigma_b b]/2, \quad (36)$$

and

$$v = \pi[\sigma_a^3 + \sigma_b^3 + 3\sigma_a^2 a + 3\sigma_b^2 b - 4a^3 - 4b^3]/12, \quad (37)$$

where

$$a = l/2 + (\sigma_a - \sigma_b)^2/8l. \quad (38)$$

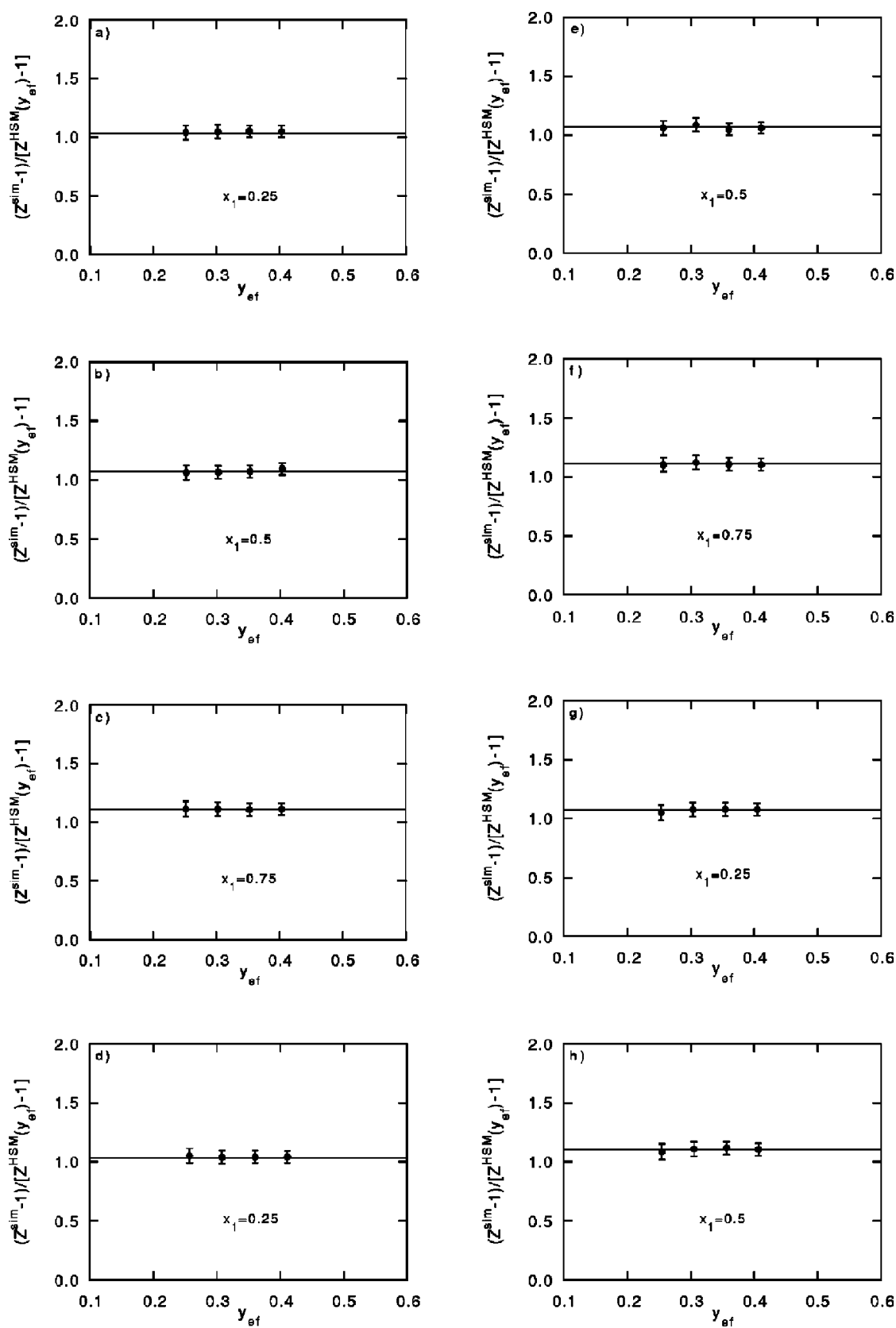


FIG. 2. Value of the ratio $(Z^{\text{HB}} - 1) / [Z^{\text{HS}}(y_{\text{mix}}^{\text{ef}}) - 1]$ for different HS+HTD mixtures as a function of the effective packing fraction $y_{\text{mix}}^{\text{ef}}$ of the mixture. Points: results from simulation data from Refs. 22 and 27. (a)–(c) correspond to $\sigma_2 = 1$ and $\sigma_{1a} = 0.5$; (d)–(f) are for $v_2 = v_1$; and (g) and (h), $\sigma_2 = 0.5$ and $\sigma_{1a} = 0.5$. In all cases $l = 0.625$. Continuous line: Eq. (28). Error bars account for the inaccuracy ΔZ in the simulation data, when known, according to $\Delta Z / [Z^{\text{HS}}(y_{\text{mix}}^{\text{ef}}) - 1]$.

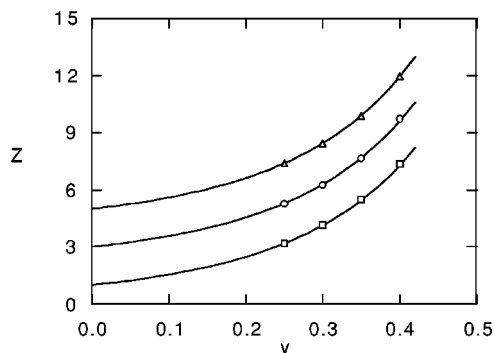


FIG. 3. Compressibility factor for HS+HTD mixtures with $\sigma_2=1$, $\sigma_{1a}=0.5$ and $l=0.625$, as a function of the effective packing fraction $y_{\text{mix}}^{\text{ef}}$ of the mixture, for mixing ratios $x_1=0.25, 0.5$, and 0.75 , respectively, from bottom to top. Points: simulation data from Refs. 22 and 27. Continuous line: Eqs. (28), (33), (39), and (41), indistinguishable at the scale of the figure. For clarity, each curve, and the corresponding simulation data, has been shifted upwards by two units with respect to the one immediately below.

Another equation of state derived from SPT is the Boublík–Nezbeda (BN) equation²²

$$Z^{\text{BN}} = \frac{1}{1-y} + \frac{rs}{\rho(1-y)^2} + \frac{qs^2(1-y/3)}{3\rho(1-y)^3}, \quad (39)$$

with

$$r = \rho \sum_i x_i R_i, \quad s = \rho \sum_i x_i S_i, \quad q = \rho \sum_i x_i R_i^2, \quad (40)$$

where R_i and S_i have the same meaning as for Eq. (33).

Finally, a successful equation of state for athermal mixtures is that derived from bonded hard-sphere theory. The BHS equation of state for a multicomponent mixture having N_m molecules is²⁸

$$Z_{\text{mix}}^{\text{BHS}} = \frac{PV}{N_m kT} = \sum_i x_m(i) N_s(i) Z^{\text{HS}} - \sum_i x_m(i) \sum_{\text{bonds}} \left[1 + \frac{\rho}{g_{jk}^{\text{HS}}(\sigma_{jk})} \left(\frac{\partial g_{jk}^{\text{HS}}(\sigma_{jk})}{\partial \rho} \right)_{T,N} \right], \quad (41)$$

where $x_m(i)$ is the mole fraction of species i whose molecules have $N_s(i)$ 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. (13). For dumbbells consisting of nonoverlapping spheres, the nonsphericity parameter is determined from Eq. (4) by using expressions (35)–(38). When spheres overlap, the molecule is replaced by an equivalent nonoverlapping one with the condition that the nonsphericity parameters of the two are equal.

Figures 3–5 compare results from Eqs (33), (39), and (41) with those from Eq. (28) and with simulation data.^{22,27} It can be seen that for most of the cases considered all three equations provide excellent accuracy, although Eq. (28) is somewhat more accurate, on the whole, than the other three

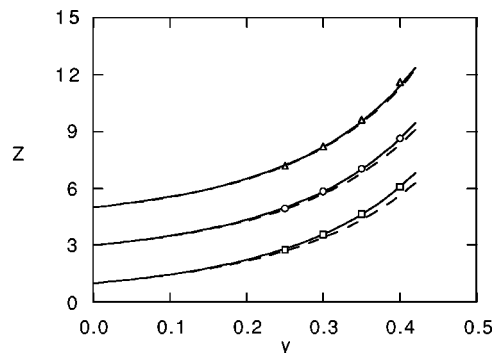


FIG. 4. As in Fig. 3 for HS+HTD mixtures with $\sigma_2=0.5$, $\sigma_{1a}=0.5$ and $l=0.625$. Continuous line: Eqs. (28), (39), and (41), indistinguishable at the scale of the figure; dashed line: Eq. (33).

as revealed by the averaged absolute deviations $D = (100/n) \sum |Z^{\text{calc}} - Z^{\text{sim}}| / Z^{\text{sim}}$, where n is the number of data points, which are 0.76%, 0.91%, 1.68%, and 0.83%, respectively, for our Eq. (28), BN equation (39), SPT equation (33), and BHS equation (41).

A question which arises is whether Eq. (28) can be extended to mixtures of molecules with a greater number of spheres. To do so, the problem to be solved is the determination of analytical expressions for the effective molecular volumes v_{ij}^{ef} . For mixtures of linear homonuclear molecules these expressions have been reported recently.²⁹ For mixtures of linear heteronuclear molecules, we can generalize the expressions given in the Appendix for mixtures of HS with HTD, in a similar way as the expressions corresponding to pure HTD fluids were generalized¹¹ to pure fluids consisting of heteronuclear triatomic molecules. The only problem which remains unsolved is the application to fluids having nonlinear molecules. The same problem is present in SPT and BHS theories because the parameter α they require must be obtained numerically.²⁸ The problem is overcome in the BHS theory by determining α for the diatomic or triatomic segments which form the molecule, although the results thus obtained for tetrahedral FHS pentaatomics seems to be rather poor.²⁸ In principle, a similar procedure, that is to divide the molecule into its constituent diatomic or triatomic segments to determine the v_{ij}^{ef} , might be useful in the context of Eq. (28), but additional work on this subject is required.

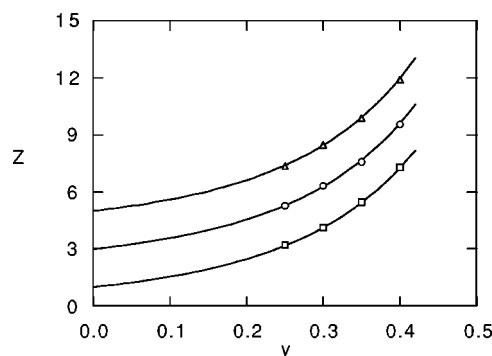
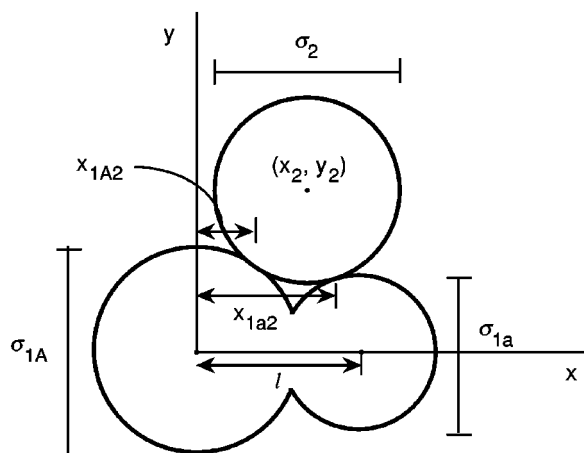


FIG. 5. As in Fig. 3 for HS+HTD mixtures with $v_2=v_1$ and $l=0.625$. Continuous line: Eqs. (28), (33), (39), and (41), indistinguishable at the scale of the figure.

FIG. 6. Definition of quantities which are relevant for the calculation of v_{12}^{ef} .

In summary, the equation of state previously developed for HCB fluid mixtures and extended to homonuclear FHS mixtures, has been generalized in this paper to mixtures of HS with HTD. To do so, we have derived expressions to obtain the geometrical parameters involved. The results agree with simulation data within the statistical uncertainty of the latter.

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APPENDIX

As stated before, the contributions v_{11}^{ef} and α_{11}^{ef} to v_m^{ef} and α_m^{ef} , respectively, can be determined from the expressions for pure HTD fluids reported in a previous paper.¹¹ The contributions $v_{21}^{\text{ef}} = v_{22}^{\text{ef}}$ are trivially determined, as they correspond to the real volume of the spheres, as well as the corresponding contributions $\alpha_{21}^{\text{ef}} = \alpha_{22}^{\text{ef}} = 1$.

To determine the contributions v_{12}^{ef} and α_{12}^{ef} to v_m^{ef} and α_m^{ef} , consider a diatomic heteronuclear molecule 1, with spheres denoted by A and a, and a sphere 2 (Fig. 6). Let us denote by x_{1A2} and x_{1a2} , respectively, the x coordinates of the contact points when sphere 2 is simultaneously touching spheres A and a. Then, the effective volume of the HTD molecule 1 as seen by sphere 2 can be obtained from

$$v_{12}^{\text{ef}} = v_{12}^{\text{rot}} + v_{1A2} + v_{1a2}, \quad (\text{A1})$$

where v_{1A2} is the volume of sphere A on the left of x_{1A2} , v_{1a2} is the volume of sphere a on the right of x_{1a2} , and v_{12}^{rot} is the volume from which is excluded any point of sphere 2, between v_{1A2} and x_{1a2} when it rotates around molecule 1 remaining in contact with spheres A and a. These volumes are given by

$$v_{12}^{\text{rot}} = \pi \{ (y_2^2 + r_2^2)(x_{1a2} - x_{1A2}) - \frac{1}{3} [(x_{1a2} - x_2)^3 - (x_{1A2} - x_2)^3] + 2y_2r_2^2 [\frac{1}{2}(\alpha_{1a2} - \alpha_{1A2}) - \frac{1}{4}(\sin 2\alpha_{1a2} - \sin 2\alpha_{1A2})] \}, \quad (\text{A2})$$

$$v_{1A2} = \pi [r_{1A}^2(x_{1A2} + r_{1A}) - \frac{1}{3}(x_{1A2}^3 + r_{1A}^3)], \quad (\text{A3})$$

$$v_{1a2} = \pi \{ (r_{1a}^2 - l^2)(l + r_{1a} - x_{1a2}) - \frac{1}{3} [(l + r_{1a}^3) - x_{1a2}^3] + l[(l + r_{1a}^2) - x_{1a2}^2] \}, \quad (\text{A4})$$

where r_i is the radius of sphere i , and

$$x_2 = [l^2 - (r_{1a} + r_2)^2 + (r_{1A} + r_2)^2] / 2l, \quad (\text{A5})$$

$$y_2 = [(r_{1A} + r_2)^2 - x_2^2]^{1/2}, \quad (\text{A6})$$

$$x_{1A2} = r_{1A}x_2 / (r_{1A} + r_2), \quad (\text{A7})$$

$$x_{1a2} = l - r_{1a}(l - x_2) / (r_{1a} + r_2), \quad (\text{A8})$$

$$\alpha_{1a2} = \arccos[(x_{1a2} - x_2) / r_2], \quad (\text{A9})$$

and

$$\alpha_{1A2} = \arccos[(x_{1A2} - x_2) / r_2]. \quad (\text{A10})$$

On the other hand, definition Eq. (10) of the effective nonsphericity parameter for linear homonuclear FHS molecules can be expressed in terms of the radius r of a sphere, instead of its diameter σ , in the form

$$\alpha_{\text{ef}} = \frac{1}{24\pi} \frac{(\partial v_m^{\text{ef}} / \partial r)(\partial^2 v_m^{\text{ef}} / \partial r^2)}{v_m}. \quad (\text{A11})$$

For the problem of interest here, this expression can be generalized as follows:

$$\alpha_{12}^{\text{ef}} = \frac{1}{24\pi} \frac{v_{12}^{\text{ef}} v_{12}^{\text{ef}''}}{v_{12}^{\text{ef}}}, \quad (\text{A12})$$

where

$$v_{12}^{\text{ef}'} = \left(\frac{\partial v_{12}^{\text{ef}}}{\partial r_{1A}} \right) + \left(\frac{\partial v_{12}^{\text{ef}}}{\partial r_{1a}} \right) + \left(\frac{\partial v_{12}^{\text{ef}}}{\partial r_2} \right), \quad (\text{A13})$$

and

$$v_{12}^{\text{ef}''} = \left(\frac{\partial^2 v_{12}^{\text{ef}}}{\partial r_{1A}^2} \right) + 2 \left(\frac{\partial^2 v_{12}^{\text{ef}}}{\partial r_{1a} \partial r_2} \right) + \left(\frac{\partial^2 v_{12}^{\text{ef}}}{\partial r_2^2} \right). \quad (\text{A14})$$

The first derivative is given by

$$v_{12}^{\text{ef}'} = v_{12}^{\text{rot}'} + v_{1A2}' + v_{1a2}', \quad (\text{A15})$$

where

$$v_{12}^{\text{rot}'} = \pi \{ 2(y_2 y_2' + r_2)(x_{1a2} - x_{1A2}) + (y_2^2 + r_2^2) \times (x_{1a2}' - x_{1A2}') - (x_{1a2} - x_2)^2 (x_{1a2}' - x_2') + (x_{1A2} - x_2)^2 (x_{1A2}' - x_2') + (y_2^2 r_2^2 + 2y_2 r_2) \times [(\alpha_{1a2} - \alpha_{1A2}) - \frac{1}{2}(\sin 2\alpha_{1a2} - \sin 2\alpha_{1A2})] + y_2 r_2^2 [(\alpha_{1a2}' - \alpha_{1A2}') - (\alpha_{1a2}' \cos 2\alpha_{1a2} - \alpha_{1A2}' \cos 2\alpha_{1A2})] \}, \quad (\text{A16})$$

$$v_{1A2}' = \pi [2r_{1A}(x_{1A2} + r_{1A}) + (r_{1A}^2 + x_{1A2}^2)x_{1A2}'], \quad (\text{A17})$$

$$v_{1a2}' = \pi [r_{1a}(2l + 2r_{1a} - 2x_{1a2} - r_{1a}x_{1a2}') + x_{1a2}'(x_{1a2} - l)^2], \quad (\text{A18})$$

with

$$x'_2 = -2(r_{1a} - r_{1A})/l, \quad (\text{A19})$$

$$y'_2 = [2(r_{1A} + r_2) - x_2 x'_2]/y_2, \quad (\text{A20})$$

$$x'_{1A2} = \frac{x_2 - l + r_{1A} x'_2}{r_{1A} + r_2} - \frac{2r_{1A}(x_2 - l)}{(r_{1A} + r_2)^2}, \quad (\text{A21})$$

$$x'_{1A2} = \frac{x_2 + r_{1A} x'_2}{r_{1A} + r_2} - \frac{2r_{1A} x_2}{(r_{1A} + r_2)^2}, \quad (\text{A22})$$

$$\alpha'_{1A2} = -\xi'/(1 - \xi^2)^{1/2}, \quad (\text{A23})$$

where

$$\xi = (x_{1a2} - x_2)/r_2, \quad (\text{A24})$$

and

$$\xi' = (x'_{1a2} - x'_2)/r_2 - (x_{1a2} - x_2)/r_2^2, \quad (\text{A25})$$

$$\alpha'_{1A2} = -\xi'/(1 - \xi^2)^{1/2}, \quad (\text{A26})$$

where

$$\xi = (x_{1A2} - x_2)/r_2, \quad (\text{A27})$$

and

$$\xi' = (x'_{1A2} - x'_2)/r_2 - (x_{1A2} - x_2)/r_2^2. \quad (\text{A28})$$

The second derivative, Eq. (A14), can be determined from Eq. (A15) in the form:

$$v''_{12}{}^{\text{ef}} = v''_{12}{}^{\text{rot}} + v''_{1A2} + v''_{1a2}, \quad (\text{A29})$$

where from Eqs. (A16)–(A28), we have

$$\begin{aligned} v''_{12}{}^{\text{rot}} = & \pi \{ 2(y_2'^2 + y_2 y_2'' + 1)(x_{1a2} - x_{1A2}) + 4(y_2 y_2' + r_2)(x'_{1a2} - x'_{1A2}) + (y_2^2 + r_2^2)(x''_{1a2} - x''_{1A2}) \\ & - 2(x_{1a2} - x_2)(x'_{1a2} - x'_2)^2 - x''_{1a2}(x_{1a2} - x_2)^2 + 2(x_{1A2} - x_2)(x'_{1A2} - x'_2) + x''_{1A2}(x_{1A2} - x_2)^2 \\ & + (y_2'' r_2^2 + 4y_2' r_2 + 2y_2)[(\alpha_{1a2} - \alpha_{1A2}) - \frac{1}{2}(\sin 2\alpha_{1a2} - \sin 2\alpha_{1A2})] + 2(y_2' r_2^2 + 2y_2 r_2) \\ & \times [(\alpha'_{1a2} - \alpha'_{1A2}) - (\alpha'_{1a2} \cos 2\alpha_{1a2} - \alpha'_{1A2} \cos 2\alpha_{1A2})] + y_2 r_2^2[(\alpha''_{1a2} - \alpha''_{1A2}) \\ & - (\alpha''_{1a2} \cos 2\alpha_{1a2} - \alpha''_{1A2} \cos 2\alpha_{1A2}) + (2\alpha_{1a2}'^2 \sin 2\alpha_{1a2} - 2\alpha_{1A2}'^2 \sin 2\alpha_{1A2})] \}, \end{aligned} \quad (\text{A30})$$

$$v''_{1A2} = \pi [2x_{1A2}(1 - x_{1A2}'^2) + 4r_{1A}(x'_{1A2} + 1) + (r_{1A}^2 - x_{1A2}^2)x''_{1A2}], \quad (\text{A31})$$

$$v''_{1a2} = \pi \{ [2(l - x_{1a2})(1 - x_{1a2}'^2) + 4r_{1a2}(1 - x_{1a2}') + [(x_{1a2} - l)^2 - r_{1a}^2]x''_{1a2}] \}, \quad (\text{A32})$$

$$x''_2 = 0, \quad (\text{A33})$$

$$y_2'' = \{ y_2(4 - x_2'^2) + y_2' [2(r_{1A} + r_2 - x_2 x'_2)] \} / y_2^2, \quad (\text{A34})$$

$$x''_{1a2} = 2 \frac{x_2'(r_{1a} + r_2) - 2(x_2 - l)}{(r_{1a} + r_2)^2} \left(1 - \frac{2r_{1a}}{r_{1a} + r_2} \right), \quad (\text{A35})$$

$$x''_{1A2} = 2 \frac{x_2'(r_{1A} + r_2) - 2x_2}{(r_{1A} + r_2)^2} \left(1 - \frac{2r_{1A}}{r_{1A} + r_2} \right), \quad (\text{A36})$$

$$\alpha''_{1a2} = -\frac{\xi \xi'^2}{(1 - \xi^2)^{3/2}} - \frac{\xi''}{(1 - \xi^2)^{1/2}}, \quad (\text{A37})$$

with

$$\xi'' = \frac{x''_{1a2}}{r_2} - 2 \left(\frac{x'_{1a2} - x'_2}{r_2^2} - \frac{x_{1a2} - x_2}{r_2^3} \right), \quad (\text{A38})$$

and

$$\alpha''_{1A2} = -\frac{\xi \xi'^2}{(1 - \xi^2)^{3/2}} - \frac{\xi''}{(1 - \xi^2)^{1/2}}, \quad (\text{A39})$$

with

$$\xi'' = \frac{x''_{1A2}}{r_2} - 2 \left(\frac{x'_{1A2} - x'_2}{r_2^2} - \frac{x_{1A2} - x_2}{r_2^3} \right). \quad (\text{A40})$$

On the other hand, the real volume v_{11} of a dumbbell, which enters in Eq. (15) is

$$v_{11} = v_{1A} + v_{1a}, \quad (\text{A41})$$

where

$$v_{1A} = \pi [r_{1A}^2(\chi + r_{1A}) - (\chi^3 + r_{1A}^3)/3], \quad (\text{A42})$$

and

$$v_{1a} = \pi \{ r_{1a}^2(l + r_{1a} - \chi) - [(l + r_{1A})^3 - \chi^3]/3 + l[(l + r_{1a})^2 - \chi^2] - l^2(l + r_{1a} - \chi) \}, \quad (\text{A43})$$

with

$$\chi = (r_{1A}^2 - r_{1a}^2 + l^2)/2l. \quad (\text{A44})$$

The preceding expressions could be readily extended to HTD binary mixtures. In this case, we will denote by l_1 the center to center distance in molecule 1 and by B and b the spheres of an HTD molecule of species 2, with center to center distance l_2 . We can apply expressions (A1)–(A10) to determine the effective volume v_{12B}^{ef} of molecule 1 as seen by sphere B by changing the role of sphere 2 to that of sphere $2B$. The effective volume v_{12b}^{ef} of molecule 1 as seen by sphere b is determined in a similar way. Then, the contribution v_{12}^{ef} can be obtained by weighting these two volumes in the form¹¹

$$v_{12}^{\text{ef}} = (S_{BA} v_{12B}^{\text{ef}} + S_{ba} v_{12b}^{\text{ef}}) / (S_{BA} + S_{ba}), \quad (\text{A45})$$

where S_{BA} is the part of the surface of a sphere B which can touch a sphere A and S_{ba} is the part of the surface of a sphere b which can touch a sphere a . S_{BA} is given by

$$S_{BA} = 2\pi r_{2B}^2 (1 + x_{2B1A}/r_{2B}), \quad (\text{A46})$$

where

$$x_{2B1A} = r_{2B} x_{1A} / (r_{1A} + r_{2B}), \quad (\text{A47})$$

with

$$x_{1A} = [l_2^2 - (r_{2B} + r_{1A})^2 + (r_{2B} + r_{1A})^2] / 2l_2. \quad (\text{A48})$$

Analogously, for S_{ba} we have

$$S_{ba} = 2\pi r_{2b}^2 [1 + (l_2 - x_{2b1a})/r_{2b}], \quad (\text{A49})$$

$$x_{2b1a} = l_2 - r_{2b}(l_2 - x_{1a}) / (r_{1a} + r_{2b}), \quad (\text{A50})$$

and

$$x_{1a} = [l_2^2 - (r_{1a} + r_{2b})^2 + (r_{1a} + r_{2b})^2] / 2l_2. \quad (\text{A51})$$

Once we have obtained the expression of v_{12}^{ef} in this way, we can derive it twice to obtain α_{12}^{ef} by means of Eq. (A12). However, we must take into account that now, instead of Eqs. (A13) and (A14) we have

$$v_{12}^{\prime \text{ef}} = \left(\frac{\partial v_{12}^{\text{ef}}}{\partial r_{1A}} \right) + \left(\frac{\partial v_{12}^{\text{ef}}}{\partial r_{1a}} \right) + \left(\frac{\partial v_{12}^{\text{ef}}}{\partial r_{2B}} \right) + \left(\frac{\partial v_{12}^{\text{ef}}}{\partial r_{2b}} \right), \quad (\text{A52})$$

and

$$v_{12}^{\prime \prime \text{ef}} = \left(\frac{\partial v_{12}^{\prime \text{ef}}}{\partial r_{1A}} \right) + \left(\frac{\partial v_{12}^{\prime \text{ef}}}{\partial r_{1a}} \right) + \left(\frac{\partial v_{12}^{\prime \text{ef}}}{\partial r_{2B}} \right) + \left(\frac{\partial v_{12}^{\prime \text{ef}}}{\partial r_{2b}} \right). \quad (\text{A53})$$

The contributions v_{21}^{ef} and α_{21}^{ef} can be determined from the same expressions by changing the roles of molecules of species 1 and 2.

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