

# Equation of State for Repulsive Models of n-Alkane Pure Fluids and Mixtures

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Theoretically-based equations of state previously developed for hard models of molecular pure fluids and mixtures are extended in this paper to repulsive models of pure n-alkane fluids and mixtures. For pure fluids, the compressibility factor is expressed in terms of a scaling of the excess compressibility factor of a hard-sphere fluid with a packing fraction equal to the effective packing fraction of the true fluid. For mixtures, the excess compressibility factor is expressed as a similar scaling of the excess compressibility factor of a hard-sphere fluid mixture. The theory requires two parameters, namely the scaling factor and the effective (averaged) molecular volume of the fluid (mixture), which can be determined from the molecular geometry. Results are in generally good agreement with available simulation data.

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**KEY WORDS:** BMCSL equation; Carnahan–Starling equation; equation of state; hard-body fluids; hard-sphere fluid.

## 1. INTRODUCTION

Much progress in our understanding of the properties of molecular fluids and fluid mixtures has been achieved in the last three decades. This is partially due to the increase in the performance of modern computers which has allowed more and more complicated models of molecular fluids to be simulated. This, in turn, has favored theoretical developments which often use simulation data to compare with theoretical predictions.

One of the most significant advances has arisen from the recognition that repulsive forces mainly determine the structure and properties of fluids. This has led to focus efforts towards the development of accurate theories for repulsive models of real molecular fluids. From these theories

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the properties of molecular fluids having attractive intermolecular interactions in addition to repulsive ones can be obtained from perturbation theories [1–6], using for the reference fluid the structural and thermodynamic properties of a repulsive model suitable to the fluid under study.

Regarding repulsive models of fluids and fluid mixtures, the most widely studied are those whose molecules are modelled as hard bodies and, for them, there are available several theories. Restricting ourselves to theories for nonspherical molecular fluids, we can mention the scaled particle theory (SPT) [7, 8] and other related approximations [9–11], integral equation theories [12–16], thermodynamic perturbation theory (TPT) [12, 17], bonded hard-sphere (BHS) theory [18–20], and generalized Flory (GF) and Flory dimer (GFD) theories [21–24].

All of these theories present limitations of one kind or another. Some of them apply to a given family of hard-body fluids or fluid mixtures, such as that consisting of flexible molecules. Others are accurate for fluids whose molecules have a reduced number of monomers, but their performance deteriorates as the number of monomers increases. Some of these theories have a degree of complexity that increases with the number of monomers of the molecules.

The situation is still more complicated for repulsive models of *n*-alkanes because, due to the torsional capability of the molecules, even a pure fluid must be considered as a mixture of conformers. Therefore, the study of these model fluids from computer simulation, and to some extent from theory too, represents a greater challenge as compared with other polyatomic fluids with lower molecular complexity.

In spite of this, considerable attention has been paid in the last decade to these kinds of model fluids and mixtures [25–30]. This has led very recently [31, 32] to the development of a perturbation theory for *n*-alkane fluid mixtures with realistic potentials which provides qualitative agreement with experimental data.

Within this context, the development of reliable equations of state for the reference systems, namely the repulsive models of pure and mixed *n*-alkanes, acquires special interest. This is the aim of this paper, where an equation of state which has proved to be accurate for a wide variety of hard-body fluids [33] is extended to repulsive models of pure *n*-alkane fluids. On the basis of this, an equation of state for *n*-alkane fluid mixtures is also derived following the procedure previously used for other hard-body fluid mixtures [34, 35] consisting of simpler molecules. In Section 2, the derivation of the equations of state for pure hard-body fluids and fluid mixtures is summarized. In Section 3, the equations are applied to models of pure and mixed *n*-alkane fluids and results are compared with available simulation data and with the results obtained from several other equations

of state used for hard-body fluids. Results are discussed in Section 4, where the possible extension to real n-alkane fluids is also analyzed.

## 2. THEORY

### 2.1. Pure Hard-Body Fluids

The virial equation for a hard-sphere (HS) fluid can be expressed in the form,

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

where  $\rho = N/V$  is the number density,  $\sigma$  is the diameter of a sphere, and  $g^{HS}(0)$  is the contact value of the pair correlation function. The preceding equation can be expressed in an alternative way,

$$Z^{HS} = 1 + \frac{1}{6} \rho S_{1+2} \sigma g^{HS}(0). \quad (2)$$

Here,  $S_{1+2} = 4\pi\sigma^2$  is the surface determined by the center of sphere 2 when it moves around sphere 1 with the two spheres remaining in contact, and  $\sigma$  can be considered as the center-to-center distance between the two spheres in contact.

A similar expression applies [36] to a fluid consisting of hard-convex-body (HCB) molecules. However, in this case the contact pair correlation function and the contact distance depend on the relative orientations of the two molecules in contact, so that they must be expressed as averaged quantities. Therefore

$$Z^{HCB} = 1 + \frac{1}{6} \rho S_{1+2} \sigma^{av} g^{av}(0). \quad (3)$$

In this case, for equal molecules  $S_{1+2} = 2S + 8\pi R^2$ , where  $S$  is the surface area of the molecule and  $R$  its mean radius of curvature. On the other hand,  $\sigma^{av} = \langle \mathbf{r}_{12} \cdot \mathbf{v} \rangle$ , where  $\mathbf{r}_{12}$  is the position vector from a reference point in molecule 1 to another in molecule 2,  $\mathbf{v}$  is the unit vector normal to the surface at the contact point, and the angular brackets mean an average.

If we consider a fluid of hard spheres with the same density  $\rho$  and the same molecular volume  $v$  as the HCB fluid, the ratio of the excess compressibility factor of the two fluids is

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

where we have introduced the nonsphericity parameter  $\alpha = RS/3v$ .

In the low density limit the compressibility factors involved in Eq. (4) can be expressed as  $Z^{HCB} \simeq 1 + B^{*HCB}\eta$  and  $Z^{HS} \simeq 1 + B^{*HS}\eta$ , where  $B^{*HCB} = 1 + 3\alpha$  is the exact second virial coefficient of the HCB fluid and  $B^{*HS} = 4$  that of the HS fluid. In the same limit,  $g^{av}(0) = 1$  and  $\sigma^{av} = \sigma_0^{av}$ . On the other hand,  $R$ ,  $v$ , and  $\alpha$  can be calculated exactly from geometry for HCB molecules [37, 38]. Then, Eq. (4) allows us to obtain the ratio  $\sigma_0^{av}/2R$ . This ratio is obviously 1 for hard spheres, that is, for  $\alpha = 1$ . For nonspherical molecules, it is found that the ratio decreases as anisotropy increases and, for example,  $\sigma_0^{av}/2R \simeq 0.8$  for  $\alpha \simeq 1.5$ . As density increases, simulation data [11, 39–41] for fluids consisting of moderately nonspherical HCB molecules show that the ratio  $\sigma^{av}/2R$  slowly decreases below its low density limiting value whereas the opposite behavior holds for the ratio  $g^{av}(0)/g^{HS}(0)$ . Therefore, for moderate to high densities, the contact values of the two correlation functions scale approximately as [33]

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

Strictly speaking, the ratio  $\sigma^{av}(0) g^{av}(0)/2Rg^{HS}(0)$  is slightly lower than 1. However, we can retain the simple scaling of Eq. (5) if we introduce into Eq. (4) the approximation  $(4/3)\pi R^3 \simeq RS$ , which is exact for hard spheres. This reduces the right-hand side of Eq. (4) simply to  $\alpha$ .

Then, by allowing the right-hand side of Eq. (4) to switch between the low and high density behaviors, we can express the equation of state of a HCB fluid in the form,

$$Z^{HCB} = 1 + \Delta B^*\eta + \alpha(Z^{HS} - 1), \quad (6)$$

where  $\Delta B^* = B^* - 4\alpha = 1 - \alpha$ .

For a hard-sphere fluid,  $\alpha = 1$ , and Eq. (6) reduces to the equation of state of a hard-sphere fluid. The latter can be well reproduced by the Carnahan–Starling equation [42]

$$Z^{CS} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (7)$$

For values of  $\alpha$  close to 1, we can put  $\Delta B^* \simeq 0$ , and Eq. (6) reduces to

$$Z^{HCB} = 1 + \alpha(Z^{HS} - 1). \quad (8)$$

An equivalent expression has been derived [43] on the basis of a modified cell theory for HCB fluids. A similar expression has been proposed [44]

for hard-chain molecular fluids, using instead of  $\alpha$  a parameter  $c$  which is a function of  $\alpha$ .

On the other hand, if the low density behavior could be extended to high densities, the final expression of the equation of state would be similar to Eq. (8), but using  $B^*/4$  instead of  $\alpha$ . This is the equation of state which results from the Parsons–Lee [45–47] theory applied to the isotropic fluid.

However, it has been shown [33] that for nonconvex hard-body fluids it is necessary to introduce the effective packing fraction  $\eta^{ef} = \rho v^{ef}$ , where  $v^{ef}$  is the effective molecular volume, instead of the packing fraction  $\eta$ . This effective molecular volume is defined as the volume that a molecule excludes to any point of another molecule. For HCB molecules, the effective and real molecular volumes are equal, but for hard nonconvex molecules, the former is slightly higher than the latter. The use of the effective packing fraction in combination with the Parsons–Lee theory results in a considerable improvement in the accuracy of the equation of state for linear fused hard-sphere chains, as found very recently [48].

In addition to the effective molecular volume, an effective nonsphericity parameter  $\alpha^{ef}$  must be introduced into Eq. (6) instead of  $\alpha$ . However, because  $R$  is ill-defined for hard nonconvex molecules, the effective nonsphericity parameter cannot be obtained for them in the same form as for HCB molecules. However, for polyatomic molecules consisting of  $n$  equal-sized spheres of diameter  $\sigma$  and center-to-center distance  $l$ , we can use an alternative definition [49] in the form

$$\alpha^{ef} = \frac{1}{3\pi} \frac{(\partial v^{ef} / \partial \sigma)_l (\partial^2 v^{ef} / \partial \sigma^2)_l}{v^{ef}}. \quad (9)$$

With these modifications, the equation of state, for both convex and nonconvex hard-body (HB) fluids, reads

$$Z^{HB} = 1 + \Delta B^{*ef} \eta^{ef} + \alpha_{ef} [Z^{HS}(\eta^{ef}) - 1], \quad (10)$$

where  $\Delta B^{*ef} = B^*(\eta^{ef}) - 4\alpha^{ef}$ , with  $B^*(\eta^{ef}) = B^*(\eta) v / v^{ef}$ , and  $B^*(\eta) \neq 1 + 3\alpha$  for nonconvex molecules. The notations  $B^*(\eta)$  and  $B^*(\eta^{ef})$  indicate the second virial coefficients in the expansions of the compressibility factor in a power series of the packing fraction  $\eta$  and in a power series of the effective packing fraction  $\eta^{ef}$ , respectively.

## 2.2. Hard-Body Fluid Mixtures

Consider now a mixture of HCB molecules at high densities. If we consider separately each of the fluids which form the mixture as a pure

fluid, its excess compressibility factor will scale, with respect to the excess compressibility factor of a HS fluid with the same packing fraction, in the form seen before. For species  $i$  we will have

$$\frac{Z_{ii} - 1}{\alpha_{ii}} = Z^{HS}(\eta_{ii}) - 1. \quad (11)$$

Each of these “scaled” fluids behaves like a hard-sphere fluid. Therefore, when they are mixed together, the mixture will behave as a hard-sphere mixture. Then introducing a suitable scaling parameter  $\alpha_{mix}$  for the mixture, we can write

$$\frac{Z_{mix}^{HCB} - 1}{\alpha_{mix}} = Z_{mix}^{HS}(\eta_{mix}) - 1. \quad (12)$$

In this expression,  $Z_{mix}^{HS}$  is the compressibility factor of a hard-sphere fluid mixture and  $\eta_{mix} = \rho v_{mix}$  is the packing fraction of the mixture. The average volume of a molecule in the mixture is

$$v_{mix} = \sum_i \sum_j x_i x_j v_{ij}. \quad (13)$$

In Eq. (12), for the compressibility factor of the hard-sphere mixture, we can take the Boublík–Mansoori–Carnahan–Starling–Leland equation [50, 51]

$$Z_{mix}^{HS} = \frac{6}{\pi\rho} \left( \frac{\zeta_0}{1-\zeta_3} + \frac{3\zeta_1\zeta_2}{(1-\zeta_3)^2} + \frac{3\zeta_2^3}{(1-\zeta_3)^3} - \frac{\zeta_3\zeta_2^3}{(1-\zeta_3)^3} \right), \quad (14)$$

in which

$$\zeta_l = \frac{\pi\rho}{6} \sum_i x_i (\sigma_i)^l. \quad (15)$$

where  $\sigma_i$  is the diameter of spheres of component  $i$  and  $\rho$  is the total number density.

To determine the parameter  $\alpha_{mix}$  in Eq. (12), we will use a simple argument. Let us assume that the equation of state of both the HCB fluid mixture and the reference HS fluid mixture could be obtained from a simple  $n$ -fluid model [52], with  $n$  equal to the number of different interactions  $ij$ , from the equations of state of the corresponding pure fluids. Then, from Eq. (8) we will have

$$Z_{mix}^{HCB} = 1 + \sum_i \sum_j \alpha_{ij} [Z^{HS}(\eta_{ij}) - 1], \quad (16)$$

and

$$Z_{mix}^{HS} = 1 + \sum_i \sum_j [Z^{HS}(\eta_{ij}) - 1], \quad (17)$$

respectively, where the last equation is obtained from Eq. (16) with  $\alpha_{ij} = 1$  for every  $i$  and  $j$ .

The low density expansions of the last two equations to the first order are

$$Z_{mix}^{HCB} - 1 \approx \sum_i \sum_j \alpha_{ij} 4\eta_{ij} = 4\eta_{mix} \sum_i \sum_j \alpha_{ij} x_i x_j \frac{v_{ij}}{v_{mix}}, \quad (18)$$

and

$$Z_{mix}^{HS} - 1 \approx 4\eta_{mix} \sum_i \sum_j x_i x_j \frac{v_{ij}}{v_{mix}} = 4\eta_{mix}, \quad (19)$$

where we have taken into account Eq. (13).

On the other hand, if introduce the last result into Eq. (12), we obtain

$$Z_{mix}^{HCB} - 1 \approx \alpha_{mix} 4\eta_{mix}. \quad (20)$$

Comparison of this result with Eq. (18) gives

$$\alpha_{mix} = \sum_i \sum_j x_i x_j \alpha_{ij} \frac{v_{ij}}{v_{mix}}. \quad (21)$$

To derive this result, we have used Eqs. (16) and (17), instead of Eqs. (12) and (14) as we ought to have done. Nevertheless, Eqs. (16) and (17) are related one to another in the same way as Eqs. (12) and (14), and it is expected that, at least at low densities, the scaling factor will be the same. However, the simple scaling law of Eq. (12) is expected to hold for moderate to high densities, as in the pure fluid. Moreover, at higher densities, the scaling between Eqs. (16) and (17) is density dependent, while  $\alpha_{mix}$  is expected to be a constant for a given mixture. Therefore, we will take Eq. (21) as an approximate result. The fact that the ratio  $(Z_{mix}^{HCB} - 1)/(Z_{mix}^{HS} - 1)$  is essentially independent of density for a variety of HCB fluid mixtures [34] and that the value of the ratio is well reproduced by Eq. (21) confirms the validity of that assumption. Strictly speaking, however, at low enough densities, the behaviour of the ratio is governed by the ratio of the second virial coefficients as in the pure fluid case. To take

into account the low and high density behaviors, we write the equation of state for HCB fluid mixtures in the form

$$Z_{mix}^{HCB} = 1 + \Delta B_{mix}^* \eta_{mix} + \alpha_{mix} [Z_{mix}^{HS}(\eta_{mix}) - 1], \quad (22)$$

where  $\Delta B_{mix}^* = B_{mix}^{*HCB} - \alpha_{mix} B_{mix}^{*HS}$ . Equation (22) reduces to Eq. (6) for a pure HCB fluid, and to the compressibility factor of a HS fluid mixture for a mixture of hard spheres, since in this case  $\Delta B_{mix}^* = 0$ ,  $\alpha_{ij} = 1$  for every  $i$  and  $j$  and, from Eq. (21),  $\alpha_{mix} = 1$ .

Equation (22) can be generalized to the case in which at least one of the species in the mixture consists of nonconvex molecules by means of introducing effective parameters. Then the general equation of state for hard-body fluid mixtures is

$$Z_{mix}^{HB} = 1 + \Delta B_{mix}^{*ef} \eta_{mix}^{ef} + \alpha_{mix}^{ef} [Z_{mix}^{HS}(\eta_{mix}^{ef}) - 1], \quad (23)$$

where  $\eta_{mix}^{ef} = \rho v_{mix}^{ef}$ , with

$$v_{mix}^{ef} = \sum_i \sum_j x_i x_j v_{ij}^{ef}, \quad (24)$$

$$\alpha_{mix}^{ef} = \sum_i \sum_j x_i x_j \alpha_{ij}^{ef} \frac{v_{ij}^{ef}}{v_{mix}^{ef}}, \quad (25)$$

and  $\Delta B_{mix}^{*ef} = B_{mix}^{*HB}(\eta_{mix}^{ef}) - \alpha_{mix}^{ef} B_{mix}^{*HS}(\eta_{mix}^{ef})$ , where  $B_{mix}^{*HB}(\eta_{mix}^{ef})$  is the second virial coefficient of the mixture in the expansion of the compressibility factor in a power series of  $\eta_{mix}^{ef}$ , and is related to the second virial coefficient  $B_{mix}^{*HB}(\eta_{mix})$  in the expansion of the compressibility factor in a power series of the packing fraction  $\eta_{mix}$  in the form  $B_{mix}^{*HB}(\eta_{mix}^{ef}) = B_{mix}^{*HB}(\eta_{mix}) v_{mix} / v_{mix}^{ef}$ .

Equation (23) applies to both convex and nonconvex molecules. However, there is a difference in the way it must be applied depending on the type of molecules. For a convex molecule of species  $i$ , its effective volume as "seen" by a molecule of species  $j$  is equal to the real volume of the former, that is  $v_{ij}^{ef} = v_{ii}$ , and similarly  $\alpha_{ij}^{ef} = \alpha_{ii}$ . For a nonconvex molecule, this is not the case in general, because the volume it excludes to another molecule depends on the geometry of both molecules. As a consequence, the parameters for a mixture can be determined from the parameters of the pure fluids that form the mixture in general only when all molecules are convex. For this reason, if Eq. (14) is to be used for  $Z_{mix}^{HS}$  in Eq. (23), it is necessary to introduce a small modification in the definition, Eq. (15), of the parameters  $\zeta_l$  in the form,

$$\zeta_l = \frac{\pi \rho}{6} \sum_i \sum_j x_i x_j (\sigma_{ij})^l, \quad (26)$$

where  $\sigma_{ij} = [(6/\pi) v_{ij}^{ef}]^{1/3}$ .



For many mixtures,  $\Delta B_{mix}^{*ef}$  is close to zero and can be neglected. The equation of state Eq. (23), or its simplified form which results from taking  $\Delta B_{mix}^{*ef} = 0$ , in combination with Eq. (14) for the reference HS fluid mixture, provides [34, 35] excellent agreement with simulation data.

### 3. APPLICATION TO *n*-ALKANE PURE FLUIDS AND MIXTURES

Computer simulations for hard models of n-alkanes have been performed by Monson et al. [57, 29]. These authors consider models of n-alkanes consisting of  $n$  hard spheres with  $n = 3$  to 8 with reduced center-to-center distances  $l^* = 0.4$ , bond angles  $\omega = 109.47^\circ$ , and several torsional potentials (for  $n \geq 4$ ) denoted as models I, II, and III in Ref. 29. Results were reported in the form of equations fitted to the simulation data. Among these models, we have considered the results corresponding to model II, because it is the most suitable candidate to be treated approximately as a fluid consisting of rigid molecules as we will do in the present paper.

On the other hand, Vega et al. [58] have performed computer simulations of repulsive models of pure n-alkanes, with  $n = 6, 7, 8, 12, 16$ , and 30, as well as two equimolar  $n-m$  mixtures with  $n-m = 10-6$  and  $12-4$ . Molecules were modelled as  $n$  sites with intramolecular and intermolecular interactions governed by a WCA-type potential

$$u^{WCA} = \begin{cases} 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + \epsilon, & r < 2^{1/6}\sigma \\ 0, & r > 2^{1/6}\sigma, \end{cases} \quad (27)$$

with  $\epsilon/k = 72$  K,  $\sigma = 3.923$  Å, effective diameter  $d = 3.7109$  Å, as determined from the Barker-Henderson [59] procedure, bond-angle  $\omega = 109.5^\circ$ , and center-to-center distance  $l = 1.53$  Å. The temperature in the simulations was set to  $T = 366.88$  K, and the molecules were allowed to adopt different conformations by means of a torsional potential. In the present paper, these molecules will be approximated by fused hard spheres with diameters  $d$  and reduced center-to-center distances  $l^* = l/d = 0.4123$ .

In order to apply Eq. (10) to these model fluids, we need to determine the parameters which enter in this equation, namely, molecular volume  $v$ , effective molecular volume  $v^{ef}$ , effective nonsphericity parameter  $\alpha^{ef}$ , and second virial coefficient  $B^*$ .

For a pure fluid of linear homonuclear molecules, each of them consisting of  $n$  equal-sized spheres of diameter  $\sigma$  with center-to-center distance

$l$ , the effective nonsphericity parameter  $\alpha^{ef}$  has been defined [49] in the form of Eq. (9) with the effective molecular volume  $v^{ef}$  given by [49]

$$v^{ef} = \frac{\pi\sigma^3}{6} \left[ 1 + 3L^* - \frac{L^{*3}}{2(n-1)^2} - 3(n-1)h^*\theta \right], \quad (28)$$

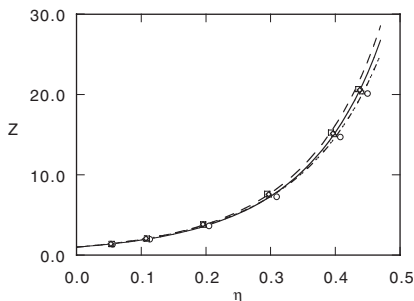
where  $L^* = L/\sigma = (n-1)l^*$ ,  $l^* = l/\sigma$ ,  $h^* = h/\sigma = (1-l^{*2}/4)^{1/2}$  and  $\theta = \sin^{-1}(l^*/2)$ , so that

$$\left( \frac{\partial v^{ef}}{\partial \sigma} \right)_l = \frac{\pi\sigma^2}{2} \left[ 1 + \frac{5L^*}{2} - 3(n-1)h^*\theta - \frac{L^{*2}\theta}{4(n-1)h^*} \right], \quad (29)$$

and

$$\begin{aligned} \left( \frac{\partial^2 v^{ef}}{\partial \sigma^2} \right)_l = \pi\sigma \left[ 1 + 2L^* - 3(n-1)h^*\theta - \frac{3L^{*2}\theta}{8(n-1)h^*} \right. \\ \left. + \frac{L^{*3}}{16(n-1)^2 h^{*2}} + \frac{L^{*4}\theta}{32(n-1)^3 h^{*3}} \right]. \end{aligned} \quad (30)$$

A more general procedure to obtain the effective molecular volume for nonlinear molecules has been developed by Connolly [53, 54]. However, definition Eq. (9) seems not to be appropriate for nonlinear molecules [55] when the effective molecular volume is determined in this way. A better prescription consists of using definition Eq. (9) with the effective molecular volume determined from Eq. (28) as for linear molecules, but using the effective molecular volume for the nonlinear molecule, as determined from the procedure of Connolly to determine the effective packing fraction  $\eta^{ef}$ . This is illustrated in Fig. 1, where the compressibility factor for hard homonuclear nonlinear triatomic molecular fluids, as determined from Eq. (10) with  $v^{ef}$  and  $\alpha^{ef}$  determined in this way and using for  $B^*$  the numerical values reported in Ref. 55, are compared with simulation data [56]. We can see that, except perhaps for the lowest value of the bond angle  $\omega$ , the agreement between theory and simulation is fairly good. Therefore, we have adopted the same criterion to determine  $v^{ef}$  and  $\alpha^{ef}$  for the repulsive models of n-alkanes considered here. However, we must mention the fact that, as we will see later, for the fluids considered in this paper, effective molecular volumes calculated from the Connolly procedure are nearly identical to those calculated from Eq. (28) for linear molecules. Therefore, the latter should be preferred as it is much simpler to use than the Connolly procedure.



**Fig. 1.** Equation of state for hard homonuclear nonlinear triatomic molecular fluids. Points: simulation data [56] for bond angles  $\omega = 60^\circ$  (circles),  $\omega = 90^\circ$  (squares),  $\omega = 120^\circ$  (triangles), and  $\omega = 150^\circ$  (diamonds). Continuous, dashed, dash-dotted, and dotted curves are the results from Eq. (10) for the same bond angles.

On the other hand, values of the averaged molecular volume  $v$  for the cases considered in Ref. 29 were reported in the same paper. For the cases of Refs. 57 and 58, we have used the procedure of Connolly [53, 54].

With regard to the second virial coefficient  $B^*$ , it has been shown [58] that a good estimate of the second virial coefficient for a given conformer of the n-alkane molecular models considered in that reference can be obtained from the relationship,

$$B^* = 1 + 3\alpha, \quad (31)$$

where  $\alpha = RS/3v$ , taking for  $S$  and  $v$ , the real surface area and volume, respectively, of the conformer and for the mean radius of curvature  $R$ , which is not well defined for this kind of molecules that corresponding to a parallelepiped of sides  $a$ ,  $b$ , and  $c$ ,

$$R = \frac{a+b+c}{4}, \quad (32)$$

with  $a$ ,  $b$ , and  $c$  determined in such a way that the principal moments of inertia of both, the conformer and the parallelepiped, are equal. Details of this procedure are given in the same paper as well as weighted average values of  $\alpha$  for the different conformers which form the n-alkane fluid. We have used the same procedure to determine the second virial coefficient of the models considered in Refs. 57 and 29, but considering only the all-*trans*

conformer for each  $n$  because we are not aware of the configurations present and their statistical weight. This may involve a small error in the estimate of  $\alpha$ , and therefore of  $B^*$ , which in any case should be of little effect on the resulting values of the equation of state, Eq. (10). To determine  $S$  and  $v$ , we have again used the procedure of Connolly [53, 54].

For the mixtures considered here, parameters  $v_{mix}$ ,  $v_{mix}^{ef}$ , and  $\alpha_{mix}^{ef}$ , which enter in Eq. (23), can be determined from the corresponding parameters for the pure fluids by means of Eqs. (13), (24), and (25). This is so because, for the mixtures in which we are interested here, all spheres (or effective spheres) are the same size regardless of if they belong to the same molecular species or not. Therefore,  $v_{ij}^{ef} = v_{ii}^{ef}$ ,  $v_{ji}^{ef} = v_{jj}^{ef}$ ,  $\alpha_{ij}^{ef} = \alpha_{ii}^{ef}$ , and  $\alpha_{ji}^{ef} = \alpha_{jj}^{ef}$ . Hence, Eqs. (13), (24), and (25), reduce to

$$v_{mix} = \sum_i x_i v_{ii}, \quad (33)$$

$$v_{mix}^{ef} = \sum_i x_i v_{ii}^{ef}, \quad (34)$$

**Table I.** Parameters Involved in Equations of State, Eqs. (10) and (23), for the Fluids Considered. Volumes Are in Units of  $\sigma^3$  (or  $d^3$ , in the Case of Molecules with Site-site Interactions Given by the WCA-Type Potential)

$n$	$l^*$	$v$	$v^{ef\ a}$	$v^{ef\ b}$	$\alpha$	$\alpha^{ef}$
3	0.4	1.1130	1.1273	1.1269	1.1876	1.1710
4	0.4	1.4059	1.4293	1.4286	1.2524	1.2903
5	0.4	1.6971	1.7314	1.7302	1.3351	1.4165
6	0.4	1.9892	2.0339	2.0319	1.4247	1.5464
7	0.4	2.2812	2.3354	2.3336	1.5212	1.6787
8	0.4	2.5733	2.6375	2.6352	1.6198	1.8125
6	0.4123	2.0272‡	2.0808	2.0743	1.3852 <sup>c</sup>	1.5697
7	0.4123	2.3263‡	2.3925	2.3844	1.4732 <sup>c</sup>	1.7068
8	0.4123	2.6252‡	2.7043	2.6946	1.5738 <sup>c</sup>	1.8453
12	0.4123	3.8220‡	3.9513	3.9351	1.9710 <sup>c</sup>	2.4075
16	0.4123	5.0191‡	5.1983	5.1757	2.3661 <sup>c</sup>	2.9755
30	0.4123	9.2083‡	9.5651	9.5176	3.6838 <sup>c</sup>	4.9763

<sup>a</sup> Exact.

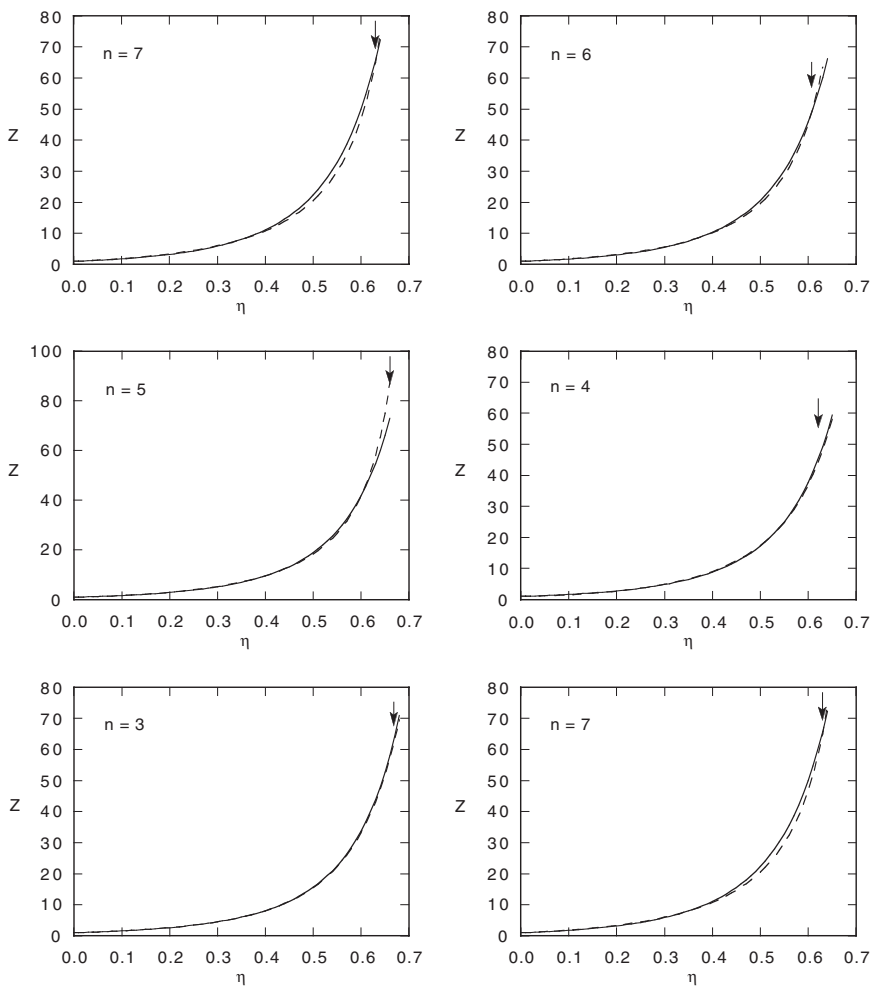
<sup>b</sup> Calculated from Eq. (28) as for a linear molecule.

<sup>c</sup> Ref. 58.

and

$$\alpha_{mix}^{ef} = \sum_i x_i \alpha_{ii}^{ef} \frac{v_{ii}^{ef}}{v_{mix}^{ef}}, \quad (35)$$

respectively.



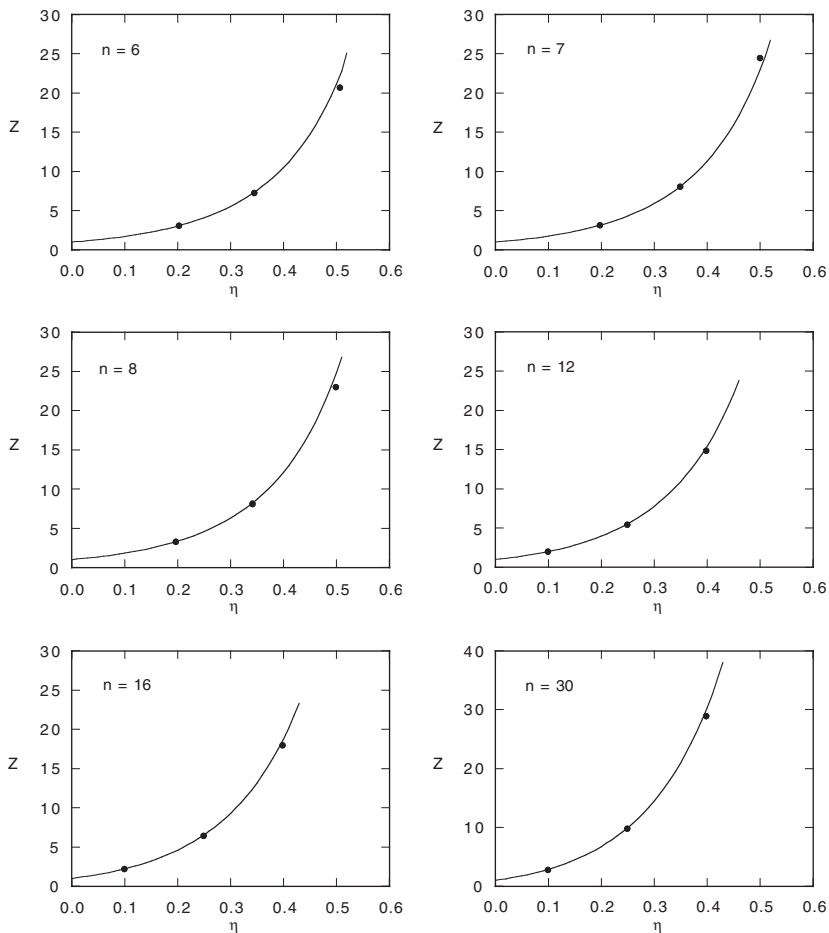
**Fig. 2.** Equation of state for hard models of n-alkane fluids. Continuous curve: Eq. (10) with or without the term  $\Delta B^{*ef} \eta^{ef}$  (both results are indistinguishable at the scale of the figure). Dashed curve: equations fitted to the simulation data, from Refs. 57 and 58. The arrows correspond to the packing fraction of the fluid in equilibrium with the solid.

Instead, the estimation of the second virial coefficient,

$$B_{mix} = \sum_i \sum_j x_i x_j B_{ij} \quad (36)$$

of the mixtures cannot be performed from the second virial coefficients of the corresponding pure fluids, because of the cross term  $B_{ij}$ . The latter, for convex molecules is given by [38]

$$B_{ij} = \frac{1}{2} (1 + 3\alpha_{ii}) v_{ii} + \frac{1}{2} (1 + 3\alpha_{jj}) v_{jj} + \Delta B, \quad (37)$$



**Fig. 3.** Equation of state for repulsive models of  $n$ -alkane fluids. Continuous curve: Eq. (10) with or without the term  $\Delta B^{*ef}\eta^{ef}$  (both results are indistinguishable at the scale of the figure). Points: simulation data, from Ref. 59.

where  $\Delta B$  depends on the geometry of both molecules and is usually small compared with the remaining terms of Eq. (37). If we assume that this expression holds approximately for nonconvex molecules too, and we take  $\Delta B \approx 0$ , then we will have

$$B_{mix}^* = \frac{B_{mix}}{v_{mix}} \approx \frac{1}{v_{mix}} \sum_i x_i B_{ii}, \quad (38)$$

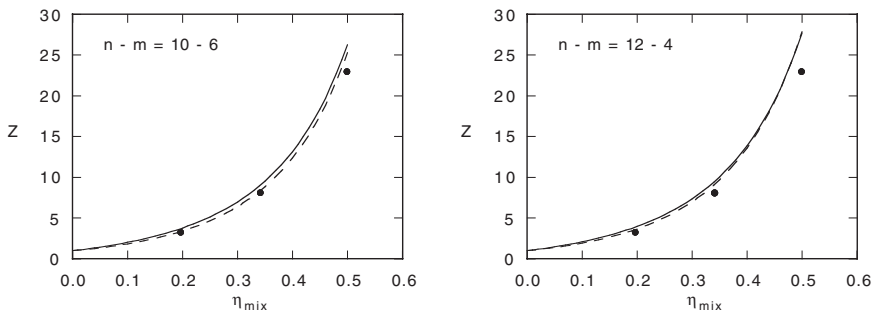
so that it can be determined approximately from the second virial coefficients of the pure fluids too.

#### 4. RESULTS AND DISCUSSION

Table I lists the values of the parameters, obtained from the procedures described in the preceding section, for the fluids of interest. One can see that the values of  $v^{ef}$  determined from the Connolly procedure and those obtained from Eq. (28) considering the n-alkane molecules as linear fused hard spheres are nearly equal, as stated before.

In Figs. 2 and 3, the results obtained from Eq. (10) for the repulsive models of n-alkane pure fluids are compared with simulation data [57–59]. One can see that the agreement between theory and simulation is quite good. The results are nearly the same if the term  $\Delta B^{*ef}\eta^{ef}$  in Eq. (10) is neglected.

Finally, in Fig. 4, results from Eq. (23) are compared with simulation data [59] for two n-alkane model mixtures. Now the influence of the term  $\Delta B_{mix}^{*ef}\eta_{mix}^{ef}$  in Eq. (23) cannot be neglected. In any case, theory overestimates the simulation data at high densities and the deviation seems to increase as the molecules in the mixture are more disparate in size. One possible



**Fig. 4.** Equation of state for repulsive models of n-alkane fluid mixtures. Continuous curve: Eq. (10) without the term  $\Delta B^{*ef}\eta^{ef}$ . Dashed curve Eq. (10). Points: simulation data, from Ref. 59.

reason is that the term  $\Delta B$  in Eq. (37) is not negligible for this kind of mixture. However, a greater variety of mixtures of n-alkanes should be analyzed before we can draw any conclusion.

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