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# Volume-Explicit Equation of State for Fused Hard Sphere Chain Fluids

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An extension of a volume-explicit equation of state for chains of tangent hard spheres to chains of fused hard spheres and their mixtures is presented. The extension was achieved by the use of a simple relationship between number of segments and nonsphericity parameter. A comparison of compressibility factors calculated using the extended equation with corresponding simulation data for hard dumbbell systems at various elongations and for fused long chains molecules and their mixtures has shown that the extended equation is reasonably accurate.

## Introduction

Large nonspherical molecules such as heavy hydrocarbons and polymers are theoretically modeled as chainlike molecules. A chain of tangent hard spheres (THS) is the simplest model of this type of molecule. Relaxation of tangency constraint in the THS chains by allowing adjacent hard spheres along the chain to overlap leads to a more realistic model which is known as fused hard sphere (FHS) chain. The FHS chain fluid serves as a useful statistical mechanical model that plays a significant role in our understanding of real molecular fluids. For instance, the possibility of molecules becoming locked together in a metastable configuration during simulation, which is a commonly encountered problem in simulation of THS molecules, is greatly reduced by treating the molecules as FHS chains.<sup>1</sup> In addition to its use in studying the effect of repulsive forces on equilibrium fluid structure of highly nonspherical systems, the FHS model also serves as a reference system in perturbation calculations of the thermodynamic properties of real systems.

There are several equations of state for fused hard sphere fluids available in the literature. Most of them are extensions of THS chains equations developed using either Wertheim's<sup>2,3</sup> first-order thermodynamic perturbation theory (TPT1) or the generalized Flory-dimer theory of Hall and co-workers.<sup>4–6</sup> Jackson and Gubbins,<sup>7</sup> Amos and Jackson,<sup>8</sup> Phan et al.,<sup>9</sup> and Zhou et al.<sup>10</sup> have all presented equation of state for FHS chains by extension of the TPT1-based equation of THS chains. The equations are similar in the sense that they all use an effective chain length  $m_{\text{eff}}$  for the FHS chain to replace the chain length  $m$  of the corresponding THS chain. The main difference between the equations proposed by the different authors lies in the expression used for the effective chain length.

Yethiraj et al.<sup>11,12</sup> and later Costa et al.<sup>13</sup> have extended the GF theory of Dickman and Hall<sup>4</sup> and the GFD theory of Honnell and Hall<sup>6</sup> for THS chains to FHS chains. They carried out the extensions by proposing various routes of identifying the properties of the reference monomer and dimer fluids that results if one breaks every bond or every other bond along a FHS chain.

Scaled particle theory (SPT), which uses a nonsphericity parameter  $\alpha$  to characterize molecular shape, provides another basis for the development of equations of state of FHS chains. Boublik<sup>14</sup> developed the so-called "improved SPT" by modifying the molecular nonsphericity  $\alpha$  to account for the noncon-

vexity of FHS chains. Largo et al.<sup>15</sup> extended their bonded hard sphere theory to fluids consisting of rigid, linear, homonuclear molecules, each of them formed by  $m$  FHS. The extension was achieved by replacing the FHS chain by an equivalent molecule formed by THS whose molecular volume and nonsphericity parameter equal that of the corresponding FHS.

Equations of state (EOS) can be identified as being either pressure explicit or volume explicit depending on whether pressure or volume, respectively, is the dependent variable. The volume-explicit form has certain advantages over the pressure-explicit one. For instance, it is numerically more convenient to use a volume-explicit EOS to carry out thermodynamic calculations/predictions in systems where a vapor phase cannot form (e.g., LLE, polymeric systems). Furthermore, many types of experimental equipments for compression of liquids operate in isothermal range with pressure as an independent variable, thus making volume-explicit equations more practically relevant. But despite these advantages, so far, volume-explicit EOS received very little attention among researchers. Notably, all the equations cited in the previous paragraphs are of the pressure-explicit type. To the best of our knowledge, the only volume-explicit EOS for FHS available in the literature is the one reported by Voertler and Nezbeda.<sup>16</sup> Their equation contains parameters which were fitted to simulation data of the compressibility factor of hard spheres and the third virial coefficient of FHS chains.

In this paper we propose an extension of a volume-explicit equation of state for THS chains, which was developed in a previous study<sup>17</sup> by one of the present authors, to system of FHS chains and their mixtures. The extended equation can serve as a useful reference in the development of equation of state for real fluids. It is hoped that the present study will be an important addition to the body of literature on equations of state of FHS chains as well as rekindle interest in the development of theoretically based volume-explicit EOS.

## Theory

As mentioned in the Introduction, our aim is to extend a previously developed EOS for THS chains to system of FHS chains. Here only minimal information for our readers' convenience will be provided because details of the development of the THS equation upon which the present study is based are available elsewhere.<sup>17,18</sup>

The first-order thermodynamic perturbation theory (TPT1), pioneered by Wertheim<sup>2,3</sup> and further developed by Chapman et al.,<sup>19</sup> is a canonical ensemble formulated theory for evaluating the thermodynamic properties of chain fluids. In a previous study

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Hamad<sup>17</sup> suggested the following as an isothermal–isobaric (NPT) ensemble analogue of the TPT1 model.

$$Z_{\text{THS}} = mZ_{\text{HS}}(T, P) - (m - 1) \left[ 1 + P \frac{\partial \ln g_{\text{NPT}}(\sigma)}{\partial P} \right] \quad (1)$$

where  $Z_{\text{THS}}$  and  $Z_{\text{HS}}$  are the compressibility factors of the THS chain and monomer fluids at the same temperature and pressure,  $m$  is the chain length, and  $g_{\text{NPT}}(\sigma)$  is the NPT ensemble contact value of the pair correlation function of the spherical units that make up the chain molecule. Here we propose to extend eq 1 to FHS by replacing the chain length  $m$  by an effective chain length,  $m_{\text{eff}}$ . Thus, the extended equations can be written as

$$Z_{\text{FHS}} = m_{\text{eff}}Z_{\text{HS}}(T, P) - (m_{\text{eff}} - 1) \left[ 1 + P \frac{\partial \ln g_{\text{NPT}}(\sigma)}{\partial P} \right] \quad (2)$$

It is important to note that while eq 1 is restricted to chain of tangent hard spheres, its generalized version given by eq 2 is expected to be applicable not only to chains of tangent hard spheres but to chains of fused hard spheres as well.

Using the expressions of  $Z_{\text{HS}}(T, P)$  and  $g_{\text{NPT}}(\sigma)$  proposed by Hamad,<sup>17</sup> eq 2 yields

$$Z_{\text{FHS}} = 1 + 4m_{\text{eff}}P^* + \frac{3}{4}m_{\text{eff}}P^* \ln \left[ \frac{3 + P^*}{3 + 25P^*} \right] + \frac{216(m_{\text{eff}} - 1)P^*}{(3 + P^*)(3 + 25P^*)\{16 + 3 \ln[(3 + P^*)/(3 + 25P^*)]\}} \quad (3)$$

where  $P^*$  is a dimensionless pressure defined as

$$P^* = P v_m / m_{\text{eff}} kT \quad (4)$$

with  $v_m$  as the molecular volume and  $k$  as the Boltzmann constant. To apply the above equation, it is necessary to have a means of evaluating the effective chain length,  $m_{\text{eff}}$ . One method of calculating the effective chain length was suggested by Walsh and Gubbins.<sup>20</sup> They relate the effective chain length to nonsphericity parameter of SPT by equating the second virial coefficient obtained from TPT1 to the one from SPT. The expression they obtained is

$$m_{\text{eff}} = 2\alpha - 1 \quad (5)$$

where  $\alpha$  is the SPT nonsphericity parameter. For spherical molecules, the nonsphericity parameter has a value of unity. Its value gives an indication of the extent of deviation of a body from the spherical shape. Thus, the problem of determining  $m_{\text{eff}}$  for molecules of FHS is reduced to that of determining the nonsphericity parameter.

For hard convex bodies, the nonsphericity parameter is exactly defined in terms of molecular surface area,  $S$ , molecular volume,  $v_m$ , and mean radius of curvature,  $R$ , as  $\alpha = RS/3v_m$ . However, for nonconvex bodies (e.g., the FHS we are dealing with here)  $\alpha$  is not a uniquely defined quantity, and therefore approximate analytical expressions or numerical methods have to be used. In a widely used approximation suggested by Boublik and Nezbeda,<sup>21</sup> the nonsphericity parameter of nonconvex body is calculated from that of an analogous convex body via the following relationship:

$$\alpha = R_{\text{cb}} S / 3v_m \quad (6)$$

Note that  $R_{\text{cb}}$  stands for the mean radius of curvature for an analogous convex body generated by figuratively wrapping the nonconvex molecule in a taut membrane, and  $S$  and  $v_m$  are respectively the surface area and volume of the actual nonconvex

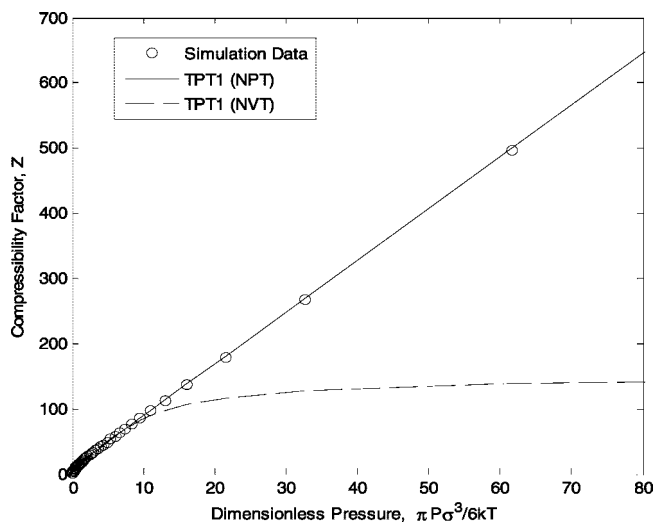


Figure 1. Compressibility factor vs reduced pressure of 5-mer hard sphere chain.

body. For rigid linear FHS chain with center to center reduced length,  $l^* = l/\sigma$ , greater than 0.5 the analogous convex body is a spherocylinder, and application of eq 6 leads to the following analytical expression for the nonsphericity parameter.<sup>22</sup>

$$\alpha = \frac{[(m - 1)l^* + 1][(m - 1)l^* + 2]}{(m - 1)(3l^* - l^{*3}) + 2} \quad (l^* \geq 0.5) \quad (7)$$

Combining eqs 5 and 7, we get

$$m_{\text{eff}} = \frac{2 + 3(m - 1)l^* + 2(m - 1)^2 l^{*2} + (m - 1)l^{*3}}{2 + 3(m - 1)l^* - (m - 1)l^{*3}} \quad (8)$$

Thus, eq 8 gives the effective chain length,  $m_{\text{eff}}$ , as an explicit nonlinear function of the actual chain length,  $m$ , and the center to center reduced length,  $l^*$ . It can easily be verified that the above equation satisfies the following exact limits:

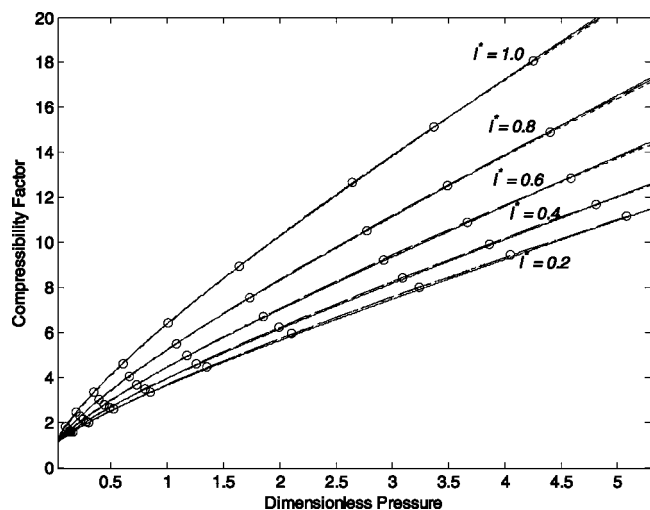
$$m_{\text{eff}} \rightarrow 1 \quad \text{as } l^* \rightarrow 0 \quad (9)$$

$$m_{\text{eff}} \rightarrow m \quad \text{as } l^* \rightarrow 1 \quad (10)$$

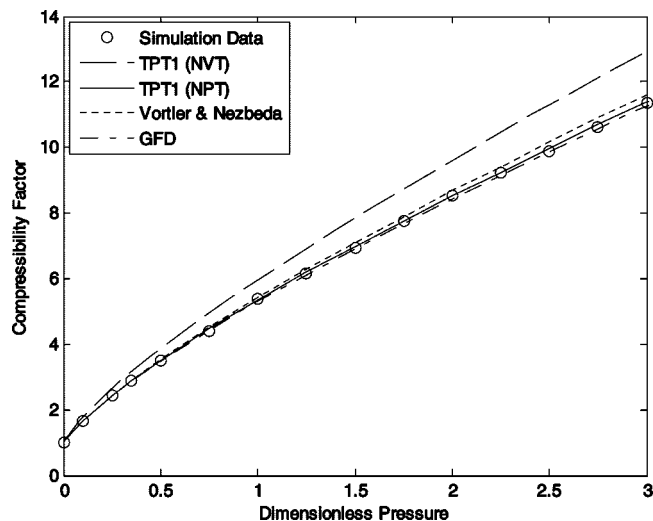
The first expression indicates that the FHS chain reduces to a single sphere as the bond length goes to zero (i.e.,  $Z_{\text{FHS}} \rightarrow Z_{\text{HS}}$  as  $l^* \rightarrow 0$ ) while the second expression shows that in the limit  $l^* \rightarrow 1$  the EOS for a FHS chain should reduce to the TPT1 equation of state for a THS chain (i.e.,  $Z_{\text{FHS}} \rightarrow Z_{\text{THS}}$  as  $l^* \rightarrow 1$ ).

**Tangent Hard Spheres.** The performance of eq 3 with  $m_{\text{eff}} = m$  in predicting compressibility factor in the isotropic region has been tested previously for THS chains with 4, 8, and 16 chain lengths, and it was found to give very accurate predictions. In a recent article<sup>23</sup> we used an available simulation data for hard spheres that extends into the metastable region to show that within the metastable region the NPT formulated EOS for hard spheres proposed by Hamad (i.e., eq 3 with  $m_{\text{eff}} = 1$ ) performs better than many of its canonical ensemble (NVT) counterparts. In the same spirit, we consider to test the performance of the volume explicit equations of state for THS chains (i.e., eq 3 with  $m_{\text{eff}} = m$ ) with the simulation data of Malanoski and Monson<sup>24</sup> at both low and high densities.

In Figure 1 we compare the predictions given by a limiting form of eq 3 and an NVT formulated EOS with simulation data for 5-mer hard chain. The NVT equation depicted in the figure is based on the TPT1 model with Carnahan–Starling EOS for

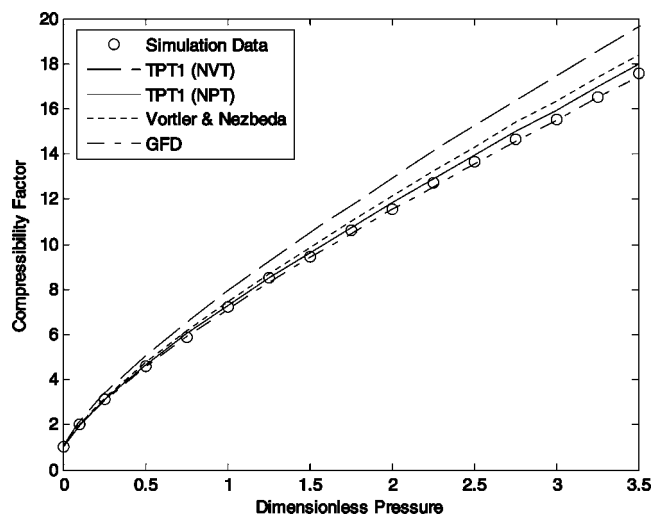


**Figure 2.** Equation of state for hard dumbbells at different elongations. Points are simulation data from the work of Tildesley and Street;<sup>25</sup> continuous line [TPT1 (NPT)], dashed line [TPT1 (NVT)], dotted line [Vortler-Nezbeda equation], dot-dashed line [GFD theory].

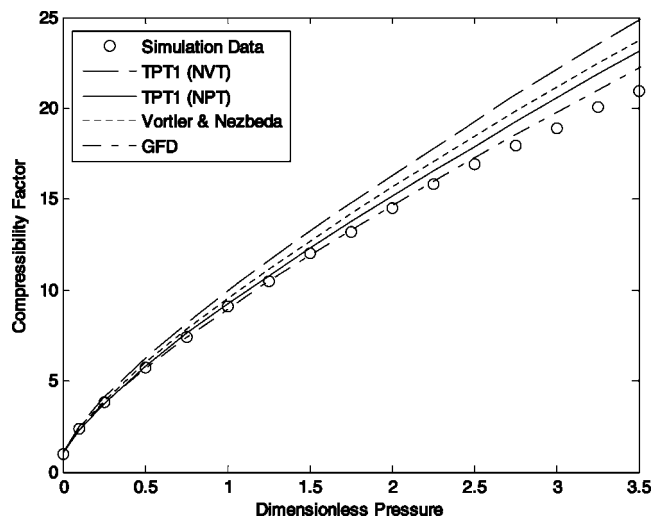


**Figure 3.** Compressibility factor of 4-mer fused hard sphere with bond length to diameter ratio  $l^* = 0.5$ .

hard spheres as the expression for  $Z_{HS}$ . As can be seen from the figure, the limiting form of eq 3 which was formulated in NPT ensemble matches the simulation data at both low and high densities. This is in sharp contrast to the similarly derived equation in the NVT ensemble, which fails to predict the simulation data at high densities. However, it is important to mention that the above result does not mean that NPT derived equations are inherently and/or generally more accurate than their NVT counterparts. As discussed in previous articles,<sup>17,23</sup> the hard sphere volume-explicit equation employed here performs better than the CS equation, especially at high pressures. Because the TPT1 model is built upon properties of the hard sphere segments (i.e.,  $Z_{HS}$  and  $g_{NPT}$ ) that form the chain molecule, it is reasonable to assume that an improvement in these properties would ultimately lead to improvement in the thermodynamic properties of the chain molecules. Perhaps, the better performance of the NPT derived equation over the equivalently NVT derived one as observed in the above comparison is mainly due to the improvement in the reference hard sphere term and the pair correlation function derived from it. However, what the above result does point out is that, apart from the convenience and practical relevance of eq 3, its

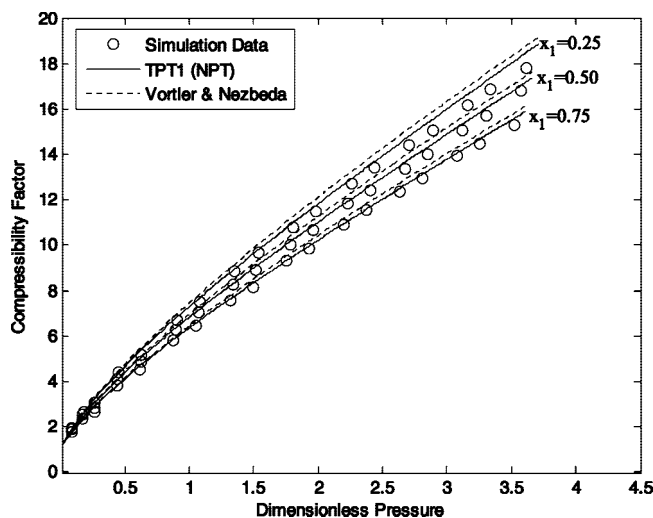


**Figure 4.** Compressibility factor of 6-mer fused hard sphere with bond length to diameter ratio  $l^* = 0.5$ .



**Figure 5.** Compressibility factor of 8-mer fused hard sphere with bond length to diameter ratio  $l^* = 0.5$ .

accuracy at high pressures makes it important for prediction of phase equilibria. This is because it is at high densities that most fluid-fluid transitions occur.



**Figure 6.** Compressibility factor of mixtures of homonuclear linear FHS with bond length to diameter ratio  $l^* = 0.5$  and  $m_1 = 4$  and  $m_2 = 6$ . Points are simulation data from the work of Largo et al.<sup>26</sup>

**Fused Hard Chains.** In this section the accuracy of the extended equation (eq 3) will be tested by presenting comparisons of its prediction of compressibility factor with simulation data of hard dumbbells and longer FHS chains. We will also compare the equation with three other equations of state.

The first equation to be used for the comparison is the one proposed by Vörtler and Nezbeda.<sup>16</sup> It is an equation of state for FHS developed by using an iterative solution of the virial equation restricted to the second order in packing fraction,  $\eta$ . Their equation is

$$Z_{\text{FHS}} = 1 + (1 + 3\alpha)\eta_0(P^*) + C_{\text{FHS}}[\eta_0(P^*)]^{1.83} \quad (11)$$

where

$$C_{\text{FHS}} = 5.66\alpha(1 - 0.045[\alpha - 1]^{1/2}\eta_0) \quad (12)$$

and

$$\eta_0(P^*) = \frac{\sqrt{1 + 4(1 + 3\alpha)P^*} - 1}{2 + 6\alpha} \quad (13)$$

The second equation is the canonical ensemble TPT1 equation for compressibility factor with effective chain segments:

$$Z_{\text{FHS}} = m_{\text{eff}}Z_{\text{HS}}(\eta) - (m_{\text{eff}} - 1)\left[1 + \eta \frac{\partial \ln g_{\text{NVT}}(\sigma)}{\partial \eta}\right] \quad (14)$$

Using the Carnahan–Starling approximation for  $Z_{\text{HS}}(\eta)$  and  $g_{\text{NVT}}(\sigma)$  gives

$$Z_{\text{FHS}} = m_{\text{eff}} \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - (m_{\text{eff}} - 1) \left( \frac{2 + 2\eta - \eta^2}{2 - 3\eta + \eta^2} \right) \quad (15)$$

In a similar fashion to eq 3, the effective chain length,  $m_{\text{eff}}$ , in eq 15 is evaluated using the expression given by eq 8.

The third equation is the GFD equation of state proposed by Honnell and Hall:<sup>6</sup>

$$Z_{\text{FHS}} = (1 + Y_n)Z_{\text{DB}} - Y_n Z_{\text{HS}} \quad (16)$$

where  $Z_{\text{HS}}$  and  $Z_{\text{DB}}$  stand for the compressibility factors of hard spheres and hard dumbbells, respectively, while  $Y_n$  is an insertion factor given by a ratio of excluded volumes of 1, 2, and  $m$  molecules. The Carnahan–Starling equation is used for evaluation of  $Z_{\text{HS}}$  while the Tildesley and Street<sup>25</sup> equation is used for  $Z_{\text{DB}}$ . In passing, we would like to mention that eqs 3 and 11 are volume-explicit EOS while eqs 15 and 16 are pressure-explicit EOS.

Let us begin with the simplest type of FHS chains, i.e. hard dumbbells. Tildesley and Street<sup>25</sup> have reported Monte Carlo simulation results of hard dumbbell system covering wide elongations and reduced densities. Figure 2 shows a comparison between their simulation data and predictions given by eqs 3, 11, 15, and 16. It is interesting that all the four equations gave very good prediction of the hard dumbbell simulation data at all reduced lengths.

Largo et al.<sup>15</sup> presented accurate Monte Carlo simulation data of fused hard sphere chain fluids with bond length to diameter ratio  $l^* = 0.5$  at different chain lengths. Figure 3 shows comparison of the simulation data reported by Largo et al. for 4-mer FHS chains with theoretical predictions given by eqs 3, 11, 15, and 16. As can be seen in the figure, predictions obtained from eqs 3, 11, and 16 are in close agreement with the simulation results. In contrast, eq 15 significantly overestimates

the simulation data. This point can be highlighted by comparing performance of the equations at high pressures, where the quality of prediction is usually low. At the highest pressure, we noticed that eq 11 overestimates the compressibility factor by more than 5%, eq 3 overestimates by about 4%, eq 16 underestimates by about 4%, and eq 15 overestimates by about 12%.

In Figures 4 and 5 we show plots of compressibility factor of FHS chains having chain lengths of 6 and 8, respectively. Similar to what was observed in Figure 3, here also we see that eqs 3 and 16 give better agreement with simulation data, followed by eq 11, while the worst performance is given by eq 15. However, it is important to mention that the accuracy of predictions given by all the equations deteriorates with increasing chain length. In the case of hard dumbbells all four equations give nearly perfect match of the simulation data, while results displayed in Figure 5 for the 8-mers show the widest deviations between simulation results and theoretical predictions. But in all the cases eq 3 shows superior capability over eq 11 in predicting the simulation data.

**Mixtures.** The extended equation presented in previous sections can be easily generalized to mixtures. All that is required is a proper definition of the mixture nonsphericity parameter,  $\alpha_{\text{mix}}$ . In order to evaluate  $\alpha_{\text{mix}}$ , we propose to use eq 6, but with the molecular volume ( $v_m$ ), surface area ( $S$ ), and radius of curvature ( $R_{\text{cb}}$ ) redefined as follows:

$$v_m = \sum x_i v_{mi} \quad (17)$$

$$S = \sum x_i S_i \quad (18)$$

$$R_{\text{cb}} = \sum x_i R_{\text{cb},i} \quad (19)$$

where  $x_i$  is the mole fraction of component  $i$  in the mixture. The definition of the dimensionless pressure remains the same (i.e.,  $P^* = P v_m / kT m_{\text{eff}}$ ), except that the effective chain length of the mixture is now obtained via the following relationship:

$$m_{\text{eff}} = \frac{2}{3} \frac{\sum x_i R_{\text{cb},i} \sum x_i S_i}{\sum x_i v_{mi}} - 1 \quad (20)$$

To test the mixture version of eq 3 based on the above proposal, we compare predictions given by the model equation with simulated compressibility factors reported in the literature. A recent literature data of equation of state for mixtures of FHS molecules was reported by Largo et al.<sup>26</sup> They performed NPT Monte Carlo simulations of binary mixtures consisting of homonuclear linear FHS molecules with  $m_1 = 4$  and  $m_2 = 6$  and mole fractions  $x_1 = 0.25, 0.50$ , and  $0.75$ . All spheres in the two molecular species were of equal diameter, and all bond length to diameter ratios were  $l^* = 0.5$ . In Figure 6, eq 3 is compared with the simulated compressibility factors and with the mixture version of the equation proposed by Vörtler and Nezbeda.<sup>16</sup> Although Vörtler and Nezbeda have used a simple mixing rule (Amagat's law) to extend their pure component equation of state to the mixture form, the predictions shown in Figure 6 were obtained by simply replacing the pure component nonsphericity parameter,  $\alpha$ , in eqs 11, 12, and 13 with the mixture nonsphericity parameter,  $\alpha_{\text{mix}}$ . This is because we noticed that using the mixture nonsphericity parameter,  $\alpha_{\text{mix}}$ , in the Voertler and Nezbeda equation gives not only similar but also more accurate results compared to the Amagat law proposition. At the three mole fractions shown in Figure 6, our



newly proposed equation gives better prediction of the simulation data than the Vörtler and Nezbeda equation.

## Conclusion

In this paper we presented a new volume-explicit equation of state for modeling the compressibility factor of fused hard sphere chains. The equation, which is useful in modeling dense fluids and liquids where the use of volume-explicit equations is most advantageous, accurately describes the behavior of hard dumbbells at various bond length to diameter ratios. The performance of the equation in predicting the compressibility factor of fused hard spheres consisting of 4-, 6-, and 8-mers with bond length to diameter ratios equal to 0.5 is better than that of the volume-explicit equation proposed by Vörtler and Nezbeda.

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