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## Equation of State for Hard Spheres and Their Mixtures in the Isotropic, Metastable, and Random Close-Packed Regions

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We present a volume-explicit equation of state for hard spheres and their mixtures that performs well in the isotropic, metastable, and random close-packed regions. The equation gives the exact second and third virial coefficients at low pressures and predicts the correct random close-packed density at infinite pressures. Comparison with simulation data showed that the equation is accurate for the isotropic, metastable, and random close-packed regions. The equation predicts phase splitting in the metastable region for molecules with large size differences.

## Introduction

Hard-body molecules are commonly used as reference systems for real fluids in perturbation theories, because of the recognition that fluid structure is determined primarily by repulsive forces. The hard sphere is the simplest model of the hard-body molecules. A recent review of 22 different analytical expressions for the compressibility factor of the hard sphere system has been presented by Mulero et al.<sup>1</sup> Although the hard-sphere model serves as a reference in perturbation theories of simple fluids, it is also used to construct the hard-core equations for chain molecules.<sup>2–8</sup>

With the exception of the equations proposed by Nezbeda and co-workers,<sup>9–11</sup> almost all commonly used theoretically based equations of state are volume-implicit (pressure is function of volume and temperature). This is mainly because the energy levels needed to evaluate the partition function are dependent on volume. In classical mechanics, the intermolecular potential is dependent on the distance between the molecules, and distance can be easily related to the volume. Another possible reason is that it is more intuitive to work with a volume occupied by molecules than count the molecular collisions with the container wall. The volume-implicit equations have the advantage that more than one phase could be represented by one equation, as is the case for most cubic equations (representing the vapor and liquid phases). Representing multiple phases by volume-explicit equations requires separate equations (roots) for each phase.

Volume-explicit equations of state have their advantages also. In one-dimensional systems, most exact results are given in the isothermal isobaric ensemble (volume-explicit).<sup>12</sup> In phase equilibrium calculations, the evaluation of density or the molar volume from a given pressure and temperature is one of the most frequently performed operations. Thus, the use of volume-implicit equations of state can slow complex chemical engineering design programs and oil reservoir simulations to a rather un-

acceptable degree. In addition, root-finding algorithms (such as the Cardanos formula for cubic roots) can lead to a significant loss of numerical precision. And, unfortunately, they do not exclude unphysical solutions, thereby making it necessary to check whether the solutions are physically meaningful. These inconveniences make the use of volume-explicit equations attractive, especially in cases where a vapor phase cannot form, such as polymer systems, liquid–liquid equilibrium, and systems at very high pressures.

In a previous study,<sup>13</sup> one of the present authors has developed an accurate volume-explicit equation of state for hard spheres. The equation is based on summation of pressure virial expansion. He later extended the equation to systems of hard chains<sup>14</sup> through utilization of contact-pair correlation functions. In this paper, we will develop an accurate mixture model that is based on the aforementioned equation. We will also test the equation in the regions of isotropic fluid, metastable phase, and random close packing.

## Theory

Hamad<sup>13</sup> proposed an accurate equation of state for hard spheres in the isothermal–isobaric ensemble. The equation, which is more accurate than the traditional Carnahan–Starling equation<sup>15</sup> at high pressures, can be expressed by

$$Z(T,P) = 1 + 4p + \frac{3p}{4} \ln\left(\frac{3+p}{3+25p}\right) \quad (1)$$

where the reduced (dimensionless) pressure is

$$p = \frac{\pi\sigma^3 P}{6kT} \quad (2)$$

$P$  is the pressure,  $T$  the temperature, and  $\sigma$  the diameter of the hard sphere. At very high pressures, this equation predicts a close-packing reduced density (which is defined as  $\eta_\infty = \pi\sigma^3\rho/6$ ) of 0.631, compared to simulation values in the range of 0.64–

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0.602.<sup>16,17</sup> The Carnahan–Starling<sup>15</sup> equation predicts a physically unattainable value of 1.

An extension of eq 1 to mixtures was suggested by Hamad.<sup>13</sup> This extension was accurate when compared to simulation data of mixtures with a size ratio up to 3. However, we later discovered a problem for mixtures with very large size differences (size ratios of  $>5$ ). The problem is caused by the quantity  $h$  in the definition of the mixture reduced pressure,

$$p = \frac{\pi h P}{6kT} \quad (3)$$

In the original extension,<sup>13</sup> the quantity  $h$ , which has units of volume, was assigned a value of  $(5S_1S_2 - S_3)/4$ , where

$$S_k = \sum x_i \sigma_i^k \quad (4)$$

This definition of  $h$  can lead to negative values of the reduced pressure for size ratios of  $>8.35$  in binary mixtures, and negative values of  $h$  lead to physically incorrect properties of hard-sphere mixtures.

To derive the correct mixture equation of state, we take a hint from volume-implicit equations. In these equations, a non-sphericity parameter,  $\alpha$ , appears in mixture equations and in pure nonspherical equations. This fact motivated us to start with the volume-explicit equation of state for pure hard chains:<sup>14</sup>

$$Z_{\text{Chain}} = 1 + 4mp + \frac{3}{4}mp \ln\left(\frac{3+p}{3+25p}\right) + \frac{216(m-1)p}{(3+p)(3+25p)\{16+3\ln[(3+p)/(3+25p)]\}} \quad (5)$$

where  $m$  is the number of segments. For mixtures of hard spheres, we keep the form of this equation and rewrite it as

$$Z = 1 + \left(4 - \frac{3}{2}b_0\right)p + \frac{3}{4}b_1p \ln\left(\frac{3+p}{3+25p}\right) + \frac{216b_0p}{(3+p)(3+25p)\{16+3\ln[(3+p)/(3+25p)]\}} \quad (6)$$

In addition to  $h$ , there are two composition- and size-dependent parameters in this equation that are yet to be determined:  $b_0$  and  $b_1$ . To recover eq 1 for pure hard spheres, we should have  $b_0 = 0$  and  $b_1 = 1$  when the mole fraction is one or when the size ratio is one.

The quantity  $h$  must be second order in regard to composition to give the correct composition dependence of all virial coefficients.<sup>13</sup> For eq 6 to give the correct second virial coefficient of mixtures of hard spheres,  $h$  takes the following form:

$$h = \frac{3S_1S_2 + S_3}{4} \quad (7)$$

This expression for  $h$  is always positive and has the correct limit of  $\sigma^3$  for pure spheres. The parameters  $b_0$  and  $b_1$  are obtained from the exact third virial coefficient and an accurate approximation to the fourth coefficient. In the pressure expansion, the two coefficients are<sup>13</sup>

$$B_3' = 3\left(\frac{\pi}{6RT}\right)^2 S_2^2(S_2 - 3S_1^2) \quad (8)$$

and

$$B_4' = \left(\frac{\pi}{6RT}\right)^3 S_2^3(54S_1^3 - 27S_1S_2 - S_3) \quad (9)$$

**Table 1. Average Absolute Deviations in the Compressibility Factor**

| equation of state      | Average Absolute Deviation, AAD (%) |                   |                              |
|------------------------|-------------------------------------|-------------------|------------------------------|
|                        | isotropic phase                     | metastable phase  | close-packed reduced density |
| Carnahan–Starling      | 0.333 <sup>a</sup>                  | 34.4 <sup>a</sup> | 1                            |
| Kolafa                 | 0.247 <sup>a</sup>                  | 34.8 <sup>a</sup> | 1                            |
| Malijevsky and Veverka | 0.228 <sup>a</sup>                  | 34.2 <sup>a</sup> | 1                            |
| Yelash and Kraska      | 0.530 <sup>a</sup>                  | 31.5 <sup>a</sup> | 3/4                          |
| Eu and Ohr             | 0.918 <sup>a</sup>                  | 40.5 <sup>a</sup> | 1                            |
| Speedy                 | N/A <sup>b</sup>                    | 10.4 <sup>a</sup> | 0.648                        |
| eq 1                   | 0.623                               | 2.77              | 0.631                        |

<sup>a</sup> Data taken from Wu and Sadus.<sup>18</sup> <sup>b</sup> Not applicable.

By requiring that the mixture equation reproduce these two coefficients, we obtain the following expressions for the two parameters:

$$b_0 = \frac{1152}{865} \frac{33\alpha^3 - 23\alpha\kappa - 13\alpha^2 + 3\kappa}{(3\alpha + 1)^3} \quad (10)$$

$$b_1 = \frac{8}{865} \frac{-729\alpha^3 + 3339\alpha\kappa + 5949\alpha^2 - 1639\kappa}{(3\alpha + 1)^3} \quad (11)$$

where  $\alpha$  has the usual definition

$$\alpha = \frac{S_1S_2}{S_3} \quad (12)$$

and

$$\kappa = \frac{S_2^3}{S_3^2} \quad (13)$$

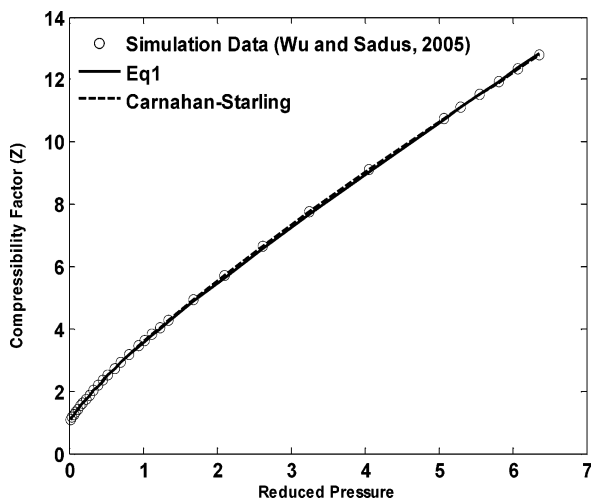
Note that, in the pure state, both  $\alpha$  and  $\kappa$  reduce to unity. The residual Gibbs energy based on eq 6 is

$$\frac{G^R}{RT} = \left(4 - \frac{3b_0}{2}\right)p + b_1 \left[ \frac{3}{4}(3+p) \ln\left(\frac{3+p}{3+25p}\right) + \frac{54}{25} \ln\left(1 + \frac{25p}{3}\right) \right] - b_0 \ln \left[ 1 + \frac{3}{16} \ln\left(\frac{3+p}{3+25p}\right) \right] \quad (14)$$

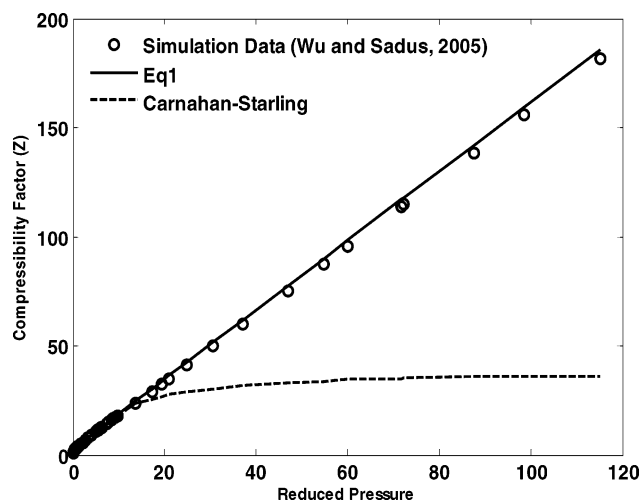
## Pure Hard Spheres

Equation 1 was tested in the past for the isotropic fluid phase, but not for the metastable phase. Recently, extensive molecular dynamics data for isotropic and metastable hard spheres were published.<sup>18</sup> Six equations of state for pure spheres were tested using this simulation data. Those equations of state were reported by Carnahan and Starling,<sup>15</sup> Kolafa,<sup>19</sup> Speedy,<sup>20</sup> Malijevsky and Veverka,<sup>21</sup> Yelash and Kraska,<sup>22</sup> and Eu and Ohr.<sup>23</sup> In the isotropic phase, the five equations that were derived for this phase fared well, with an average absolute deviation (AAD) in the range of 0.228%–0.918%, as shown in Table 1. In the metastable region, the deviations were much higher: 31.5%–40.5%. The empirical equation of Speedy,<sup>20</sup> which was suggested specifically for the metastable phase, gave an AAD of 10.8%.

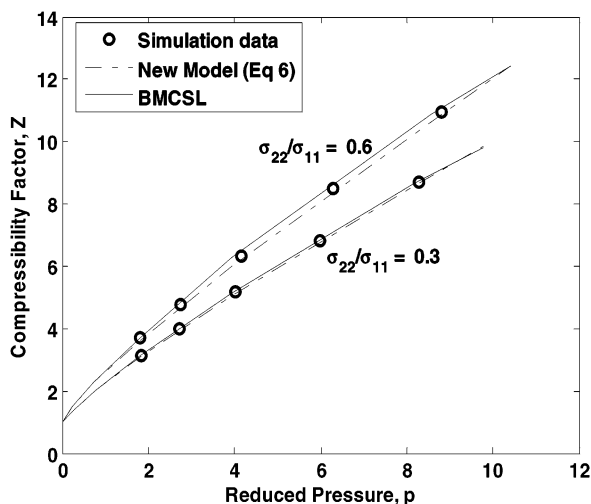
Equation 1 fared much better in the metastable phase, with an AAD of 2.77%. In the isotropic phase, eq 1 gives an AAD of 0.623%. Therefore, we can conclude that the performance of this equation in the isotropic phase is comparable to that of



**Figure 1.** Compressibility factor versus reduced pressure for hard spheres in the isotropic fluid region. Simulation from Wu and Sadus.<sup>18</sup>

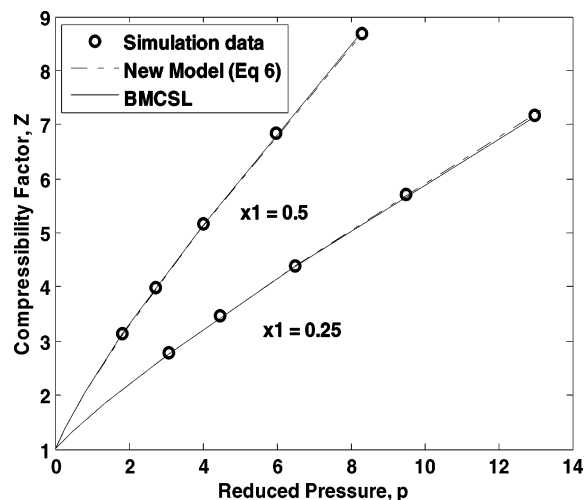


**Figure 2.** Compressibility factor versus reduced pressure for hard spheres in the isotropic and metastable regions. Simulation from Wu and Sadus.<sup>18</sup>

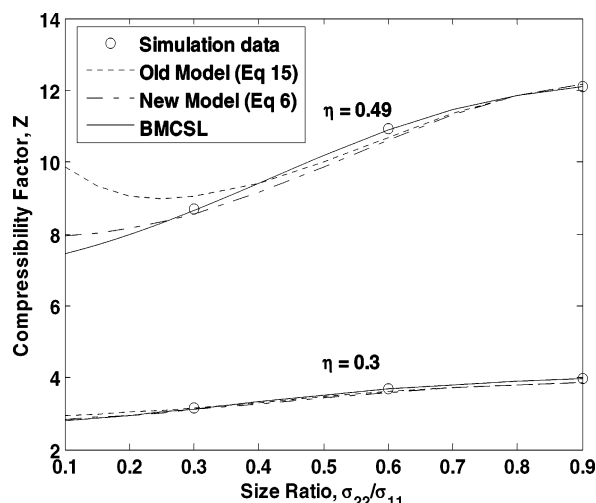


**Figure 3.** Compressibility factor versus reduced pressure for equimolar mixture of hard spheres at two different size ratios. Simulation from Barosova et al.<sup>24</sup>

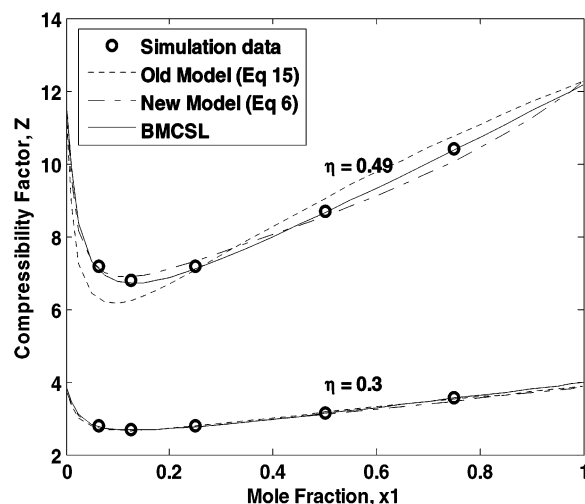
other equations, but in the metastable phase, it is much better. Figure 1 shows a comparison with the simulation data and the popular Carnahan–Starling equation in the isotropic phase, and Figure 2 shows the comparison for both the isotropic and metastable phases.



**Figure 4.** Compressibility factor versus reduced pressure for mixtures of hard spheres at a size ratio of 0.3 for two different compositions. Simulation from Barosova et al.<sup>24</sup>

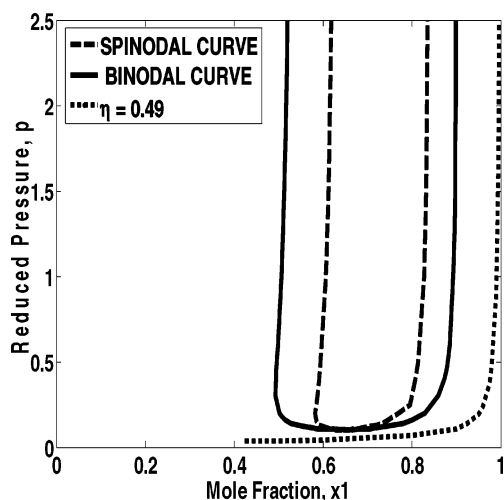


**Figure 5.** Compressibility factor of equimolar mixtures of hard spheres versus the size ratio for two different reduced densities. Simulation from Barosova et al.<sup>24</sup>



**Figure 6.** Compressibility factor versus mole fraction for mixtures of hard spheres at a size ratio of 0.3 for two different reduced densities. Simulation from Barosova et al.<sup>24</sup>

Equations of state that are developed for the fluid phase should give the density of the random close-packed phase at very high pressures. The values predicted by the six comparison



**Figure 7.** Phase diagram of mixtures of hard spheres with a size ratio of 6. The approximate freezing point curve (denoted as the dashed line) indicates that phase splitting is present in the metastable region.

equations are shown in Table 1. Five equations give physically unattainable values of unity or 0.75 (the crystalline close-packed value is 0.7405). The Speedy equation gives a reasonably accurate value of 0.648. Equation 1 gives 0.631, which is consistent with literature values in the range of 0.637–0.602.<sup>16,17</sup>

### Mixtures of Hard Spheres

In this section, we would like to compare the predictions of the new equation of state (eq 6) with simulation data. Figure 3 compares the prediction of this equation for equimolar mixtures to simulation data<sup>24</sup> and to the Boublik–Mansoori–Carnahan–Starling–Leland (BMC SL) equation.<sup>25,26</sup> Another comparison at a size ratio of 0.3 is shown in Figure 4. The two figures

indicate comparable accuracy of the two equations. Figure 4 also shows the predictions of the earlier extension of eq 1 to mixtures:

$$Z(T,P) = 1 + (1 + 3\alpha)\frac{p}{h_0} + \frac{3fp}{4h_0} \ln\left(\frac{3+p}{3+25p}\right) \quad (15)$$

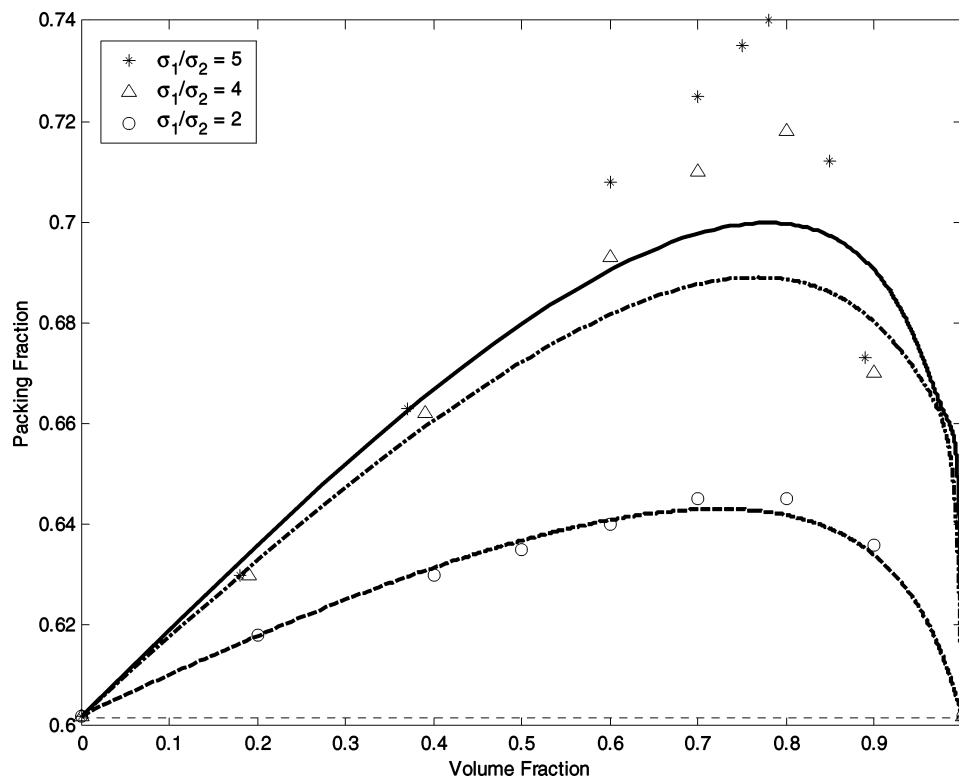
where, in this equation,  $p = \pi h_0 P / (6RT)$ ,  $h_0 = (5S_1S_2 - S_3)/4$ , and

$$f = 2 \frac{S_2^2(3S_1^2 - S_2)}{5S_1S_2 - S_3} \quad (16)$$

As mentioned previously, the problem that we discovered with this model is that  $h_0$  could become zero or negative for very large size differences, leading to incorrect physical behavior in these cases. This problem is not apparent in Figure 4. However, Figures 5 and 6 show inaccuracies that are due to this problem. The two figures also show accurate predictions by eq 6.

Recently, there has been discussion in the literature about the possibility of phase splitting in mixtures of hard spheres with large size differences. To test this possibility, we calculated the phase boundary of a mixture of hard spheres with a size ratio of 6. Figure 7 shows the binodal and spinodal curves in addition to an approximate freezing curve. The phase splitting occurs at pressures higher than the freezing pressure. This indicates that the phase splitting occurs in the metastable region and not in the isotropic region, as suggested by Dijkstra and Roij.<sup>27</sup> We would have liked to test the prediction of the mixture equation in the metastable phase, but, to our knowledge, there are no simulation data of mixtures in this region.

Our final test of the mixture equation is its ability to predict the correct close-packed density for mixtures. In the limit of



**Figure 8.** Random close-packing fraction versus volume fraction for three binary mixtures of hard spheres. Points represent the simulation data of Santiso and Mueller,<sup>17</sup> whereas the curves are the predictions from eq 17. The dashed curve at the bottom is the pure value. Note that the curves were shifted down by 0.0286 to account for the difference in the reference pure random close packing.

infinite pressure, eq 6 predicts the following packing fraction:

$$\frac{1}{\eta_{\infty}} = \frac{h}{S_3} \left[ 4 - \frac{3b_0}{2} - \frac{3}{4}(b_1 \ln 25) \right] \quad (17)$$

In Figure 8, we compare the prediction of this equation with the simulation data of Santiso and Mueller.<sup>17</sup> The predictions shown are relative to pure random close-packed values. The values reported in the literature are in the range of 0.637–0.602.<sup>16,17</sup> Equation 17 gives a pure value of 0.631, whereas Santiso and Mueller<sup>17</sup> give a value of 0.602. For this reason, we shifted the curves down by the difference: 0.0286. The predictions are observed to be accurate for a size ratio of 2, but become less accurate at larger size differences, especially at the maximum value of the close-packed density.

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### Literature Cited

- (1) Mulero, A.; Galan, C.; Cuadros, F. Equations of State for Hard Spheres. A Review of Accuracy and Applications. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4991.
- (2) Dickman, R.; Hall, C. K. Equation of State for Chain Molecules: Continuous-Space Analogue of Flory Theory. *J. Chem. Phys.* **1986**, *85*, 4108.
- (3) Wertheim, M. S. Fluids with Highly Directional Attractive Forces: I. Statistical Thermodynamics. *J. Stat. Phys.* **1984**, *35*, 19.
- (4) Wertheim, M. S. Fluids with Highly Directional Attractive Forces: IV. Equilibrium Polymerization. *J. Stat. Phys.* **1986**, *42*, 477.
- (5) Boublik, T. Equation of State of Linear Fused Hard-Sphere Models. *Mol. Phys.* **1989**, *68*, 191.
- (6) Ghonasgi, D.; Chapman, W. G. Prediction of the Properties of Model Polymer Solutions and Blends. *AIChE J.* **1994**, *40*, 878.
- (7) Chang, J.; Sandler, S. I. The Correlation Functions of Hard-Sphere Chain Fluids: Comparison of the Wertheim Integral Equation Theory with the Monte Carlo Simulation. *J. Chem. Phys.* **1995**, *102*, 437.
- (8) Sadus, R. J. Simple Equation of State for Hard-Sphere Chains. *AIChE J.* **1999**, *45*, 2454.
- (9) Nezbeda, I.; Aim, K.; Kolafa, J. On Volume-Explicit Equations of State: Hard-Body and Real Fluids. *Z. Phys. Chem. (Leipzig)* **1989**, *270*, 533.
- (10) Voertler, H. L.; Nezbeda, I. Volume-Explicit Equation of State and Excess Volume of Mixing Of Fused-Hard-Sphere Fluids. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 559.
- (11) Nezbeda, I.; Voertler, H. L. Volume-Explicit Perturbed Hard-Sphere Equation of State for Gases at High Pressures. *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 128.
- (12) Lieb, E. H.; Mattis, D. C. *Mathematical Physics in One Dimension*; Academic Press: New York, 1966.
- (13) Hamad, E. Z. Volume-Explicit Equation of State for Hard Spheres, Hard Disks, and Mixtures of Hard Spheres. *Ind. Eng. Chem. Res.* **1997**, *36*, 43850.
- (14) Hamad, E. Z. Volume-Explicit Equation of State for Hard Chains, Their Mixtures, and Copolymers. *AIChE J.* **1998**, *44*, 2766.
- (15) Carnahan, N. F.; Starling, K. E. Equation of State for Nonattracting Rigid Spheres. *J. Chem. Phys.* **1969**, *51*, 635.
- (16) Berryman, J. G. Random Close Packing Of Hard Spheres and Disks. *Phys. Rev. A* **1983**, *27*, 1053.
- (17) Santiso, E.; Muller, E. A. Dense Packing of Binary and Polydisperse Hard Spheres. *Mol. Phys.* **2002**, *100*, 2461.
- (18) Wu, G.; Sadus, R. J. Hard Sphere Compressibility Factors for Equation of State Development. *AIChE J.* **2005**, *51*, 309.
- (19) Boublik, T. Equations of State of Hard Body Fluids. *Mol. Phys.* **1986**, *59*, 371.
- (20) Speedy, R. J. On The Reproducibility of Glasses. *J. Chem. Phys.* **1994**, *100*, 6684.
- (21) Malijevsky, A.; Veverka, J. New Equations of State for Pure and Binary Hard-Sphere Fluids. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4267.
- (22) Yelash, L. V.; Kraska, T. A Generic Equation of State for the Hard-Sphere Fluid Incorporating the High-Density Limit. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3114.
- (23) Eu, B. C.; Ohr, Y. G. Thermodynamically Consistent Equation of State of Hard Sphere Fluids. *J. Chem. Phys.* **2003**, *118*, 2264.
- (24) Barosova, M.; Malijevsky, M.; Labik, S.; Smith, W. R. Computer Simulation of the Chemical Potentials of Binary Hard-Sphere Mixtures. *Mol. Phys.* **1996**, *87*, 423.
- (25) Mansoori, G. A.; Carnahan, N. F.; Starling, K. E.; Leland, T. W., Jr. Equilibrium Thermodynamic Properties of Mixture of Hard Spheres. *J. Chem. Phys.* **1971**, *54*, 1523.
- (26) Boublik, T. Hard-Sphere Equation of State. *J. Chem. Phys.* **1970**, *53*, 471.
- (27) Dijkstra, M.; Van Roij, R. Entropy-Driven Demixing In Binary Hard-Core Mixtures: From Hard Spherocylinders Towards Hard Spheres. *Phys. Rev. E* **1997**, *56*, 5594.

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