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A Simplified Thermodynamic Perturbation Theory-Dimer Equation of State for Mixtures of Hard-Sphere Chains

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ABSTRACT: The simplified thermodynamic perturbation theory-dimer (STPT-D) equation of state is generalized to mixtures of hard-sphere chains. The generalized equation contains no additional adjustable parameters, and it can be used for hard-sphere chain mixtures containing components with either identical or dissimilar hard-sphere segments. The compressibility factor predicted by the STPT-D equation of state is compared with molecular simulation data for several hard-sphere chain mixtures. Good agreement with simulation data is obtained when the ratio of hard-sphere segment diameters for the component chains is <2. For these mixtures the average absolute deviation between theory and simulation is typically 0.35%−3.5%. The accuracy of the STPT-D equation compares favorably with the results obtained for other, more complicated, hard-sphere chain equations of state.

1. Introduction

The development of accurate equations of state for macromolecules is important because they can be used, in principle, to predict all configurational thermodynamic properties. In particular, the phase transitions of fluids can be calculated. Equations of state for simple fluids have been developed[1] successfully by using hard-sphere interactions as the theoretical basis of intermolecular repulsion. The contribution from attractive interactions can often be treated as a perturbation of hard-sphere repulsion. Similarly, the concept of a chain of freely jointed hard-sphere segments can be used as the theoretical basis of an equation of state for large, nonrigid linear molecules or polymers. The usefulness of the hard-sphere chain concept has been demonstrated by several workers.[2−9] Flory's concept of excluded volume has been incorporated[2] in a reasonably accurate hard chain equation of state. Chiew[3] developed a rigorous theory for representing hard chains which has been formulated recently[4,5] into a useful equation of state for polymers. Wertheim[6] proposed a thermodynamic perturbation theory (TPT) which accommodates hard chain molecules. The TPT model is the basis of the successful statistical associating fluid theory[7] (SAFT) for real molecules. The accuracy of thermodynamic perturbation theory has been improved[8,9] by incorporating structural information for the diatomic fluid.

Recently, Sadus[10,11] proposed a simplified thermodynamic perturbation theory-dimer (STPT-D) equation of state for chains composed of m hard-sphere segments. The STPT-D equation of state predicts accurately both the compressibility and second virial coefficient molecular simulation data for chains of 4−201 hard-sphere segments. The equation also generally outperforms other equations of state such as the thermodynamic perturbation theory (TPT) equations, the Chiew equation, and the generalized Flory-dimer (GF-D) equation. The STPT-D equation has been applied only to pure components. The aim of this work is to extend the method to mixtures. The result is a relatively simple hard-sphere chain equation of state for mixtures that can be used as the theoretical basis of equations of state for real macromolecular mixtures.

2. Extension of the STPT-D Equation of State to Mixtures

The starting point for the derivation of the STPT-D equation of state is a modified TPT[8,9] equation that incorporates structural information for the diatomic fluid. The compressibility factor (Z_{m}) of a hard-sphere chain can be determined from the hard-sphere compressibility (Z_{HS}) and the site−site correlation functions at contact of both hard spheres (g_{HS}) and hard dimers (g_{HD}):

$$Z_{\mathrm{m}} = mZ_{\mathrm{HS}} - 0.5m\left(1 + \eta\frac{\partial \ln g_{\mathrm{HS}}}{\partial\eta}\right) - (0.5m - 1)\left(1 + \eta\frac{\partial \ln g_{\mathrm{HD}}}{\partial\eta}\right) \quad (1)$$

where $m \geq 2$ is the number of hard-sphere segments and $\eta = \pi m\sigma^3\rho/6$ is the packing fraction of hard spheres of a particular diameter (σ) and density (ρ). Molecular simulation data[12] for pure fluids indicate that there is a linear relationship between the hard-sphere and hard-dimer correlation functions. Therefore, Sadus[10,11] proposed that, in general,

$$g_{\mathrm{HD}} = g_{\mathrm{HS}}(\alpha\eta + c) \quad (2)$$

where α and c are the constants for a straight line. The general form of the STPT-D equation of state for pure hard-sphere chains is obtained by substituting eq 2 into eq 1.

$$Z_{\mathrm{m}} = 1 + m(Z_{\mathrm{HS}} - 1) + (1 - m)\eta\frac{\partial \ln g_{\mathrm{HS}}}{\partial\eta} + \frac{\alpha(2 - m)\eta}{2(\alpha\eta + c)} \quad (3)$$

The derivation of eq 3 is less rigorous than other hard-sphere chain equations.[7−9] Nonetheless, it has been demonstrated[10] that eq 3 predicts accurately the compressibility of pure hard-sphere chains.

The extension of eq 3 to mixtures can be achieved by using some elements of the one-fluid theory.[13] The one-fluid theory assumes that the configurational properties of the mixture are identical to a hypothetical pure fluid. The characteristic parameters of the hypothetical fluid

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are composition averages of the characteristic parameters of the pure components of the mixture. The one-fluid model has been used[1] successfully to predict the properties of a wide range of mixtures of simple molecules.

We propose the following straightforward generalization of eq 3 to mixtures of hard-sphere chains

$$Z_{\mathrm{m}}^{\mathrm{mix}} = 1 + m_{\mathrm{mix}}(Z_{\mathrm{HS}}^{\mathrm{mix}} - 1) + (1 - m_{\mathrm{mix}})\eta\frac{\partial \ln g_{\mathrm{HS}}^{\mathrm{mix}}}{\partial\eta} + \frac{\alpha_{\mathrm{mix}}(2 - m_{\mathrm{mix}})\eta}{2(\alpha_{\mathrm{mix}}\eta + c_{\mathrm{mix}})} \quad (4)$$

where $\eta = \pi m_{\mathrm{mix}}\sigma_{\mathrm{mix}}{}^3\rho/6$ is now the packing fraction of the hard-sphere chain mixture. In eq 4, the compressibility factor and correlation function of pure hard spheres have been replaced by the compressibility factor and correlation function of a mixture of hard spheres evaluated for the same packing fraction as the hard-sphere chain mixture. No simulation data are available, but we assume a linear relationship between the hard-sphere and hard-dimer correlation functions for mixtures. The chain length (m_{mix}) is obtained from a mole fraction average of the pure component properties.

$$m_{\mathrm{mix}} = \sum_{i=1}^{N} x_i m_i \quad (5)$$

Following the same procedure used[10] for the pure component version of the STPT-D equation, we can derive an equation of state for mixtures by using appropriate expressions for the compressibility factor and correlation function of a mixture of hard spheres. Boublík[14] and Mansoori et al.[15] obtained an accurate representation for the compressibility factor of an N-component mixture of hard spheres of varying diameters (σ). Their result can be expressed as

$$Z_{\mathrm{HS}}^{\mathrm{mix}} = \frac{1 + (1 - 3\beta)\eta + (1 - 3\gamma)\eta^2 - \delta\eta^3}{(1 - \eta)^3} \quad (6)$$

where

$$\beta = \frac{\sum_{j>i}^{N}\sum_{i=1}^{N-1} x_i x_j(\sigma_i + \sigma_j)(\sigma_i - \sigma_j)^2}{\sum_{i=1}^{N} x_i\sigma_i{}^3} \quad (7)$$

$$\gamma = \frac{\sum_{j>i}^{N}\sum_{i=1}^{N-1} x_i x_j\sigma_i\sigma_j(\sigma_i - \sigma_j)^2\sum_{k=1}^{N} x_k\sigma_k{}^2}{(\sum_{i=1}^{N} x_i\sigma_i{}^3)^2} \quad (8)$$

$$\delta = \frac{(\sum_{i=1}^{N} x_i\sigma_i{}^2)^3}{(\sum_{i=1}^{N} x_i\sigma_i{}^3)^2} \quad (9)$$

The above formulation of the hard-sphere mixture equation of state is equivalent to the slightly more complicated equation used by Dimitrelis and Prausnitz.[16]

To obtain a relationship for $g_{\mathrm{HS}}^{\mathrm{mix}}$, we observe that the compressibility of a mixture of hard spheres can be determined rigorously from the pair correlations functions (g_{ij}) by using the following relationship.[5,17]

$$Z_{\mathrm{HS}}^{\mathrm{mix}} = 1 + \frac{2\pi\rho}{3}\sum_{j=1}^{N}\sum_{i=1}^{N} x_i x_j\sigma_{ij}{}^3 g_{ij}(\sigma_{ij}) \quad (10)$$

From eq 10, $g_{\mathrm{HS}}^{\mathrm{mix}}$ is identified as the composition double sum of the individual pair correlation functions. Consequently, we can make the following approximation.

$$g_{\mathrm{HS}}^{\mathrm{mix}} \approx \frac{Z_{\mathrm{HS}}^{\mathrm{mix}} - 1}{4\eta} \quad (11)$$

Equation 11 is exact when the hard spheres are of unit diameter. When eq 6 is substituted into eq 11, we obtain

$$g_{\mathrm{HS}}^{\mathrm{mix}} = \frac{4 - 3\beta - (2 + 3\gamma)\eta + (1 - \delta)\eta^2}{4(1 - \eta)^3} \quad (12)$$

The STPT-D equation of state for mixtures is obtained by substituting eqs 6 and 12 into eq 4.

$$Z_{\mathrm{m}}^{\mathrm{mix}} = 1 + \frac{m_{\mathrm{mix}}[(4 - 3\beta)\eta - (2 + 3\gamma)\eta^2 + (1 - \delta)\eta^3]}{(1 - \eta)^3} + \frac{(1 - m_{\mathrm{mix}})[(10 - 9\beta - 3\gamma)\eta - (2 + 6\gamma + 2\delta)\eta^2 + (1 - \delta)\eta^3]}{(1 - \eta)[4 - 3\beta - (2 + 3\gamma)\eta + (1 - \delta)\eta^2]} + \frac{\alpha_{\mathrm{mix}}(2 - m_{\mathrm{mix}})\eta}{2(\alpha_{\mathrm{mix}}\eta + c_{\mathrm{mix}})} \quad (13)$$

In the case of pure fluids ($\beta = 0$, $\gamma = 0$, and $\delta = 1$) eq 13 becomes the pure fluid STPT-D equation reported by Sadus,[10,11] i.e.,

$$Z_{\mathrm{m}}^{\mathrm{pure}} = 1 + \frac{m(4\eta - 2\eta^2)}{(1 - \eta)^3} + \frac{(1 - m)(5\eta - 2\eta^2)}{(1 - \eta)(2 - \eta)} + \frac{\alpha(2 - m)\eta}{2(\alpha\eta + c)} \quad (14)$$

For pure fluids, suitable values of α and c were obtained[10] by comparing the second virial coefficients predicted by the STPT-D equation with molecular simulation data[18] for hard-sphere chains of varying length. A similar comparison for mixtures of hard-sphere chains cannot be made because there are no second virial coefficient simulation data for mixtures. Instead, we assume that the values of the pure component coefficients are also valid for mixtures, i.e, $\alpha_{\mathrm{mix}} = 0.7666$ and $c_{\mathrm{mix}} = 0.5$. This assumption is likely to reduce the accuracy of the calculated compressibility factor. However, in most cases the additional uncertainty will be relatively small because the contribution to the compressibility factor of the term in eq 14 involving these parameters is small compared with the contributions of the other terms.

The second virial coefficient can be obtained from the compressibility factor by using the relationship

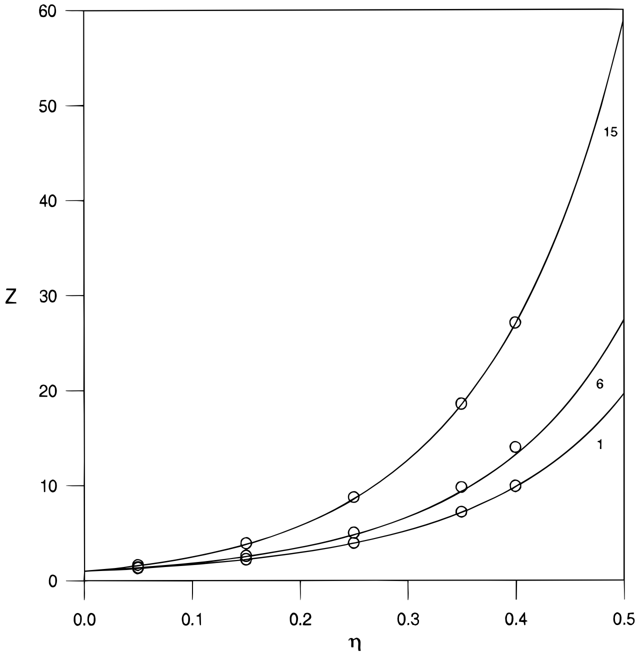

Figure 1. Comparison of the compressibility factors predicted by eq 13 (—) with simulation data[23] (○) for the equimolar hard-sphere chain mixtures 1, 6, and 15 in Table 1.

$$B_2^{\text{mix}} = \left(\frac{\partial Z_{\text{m}}^{\text{mix}}}{\partial \rho}\right)_{\rho=0} \qquad (15)$$

For the compressibility given by the STPT-D equation of state (eq 13), we obtain the following result for mixtures.

$$\frac{B_2^{\text{mix}}}{m_{\text{mix}}{}^2\sigma_{\text{mix}}{}^3} = \frac{\pi}{6}\left\{4 - 3\beta + \frac{(10 - 9\beta - 3\gamma)}{4 - 3\beta}\left(\frac{1}{m_{\text{mix}}} - 1\right) + \frac{\alpha_{\text{mix}}}{c_{\text{mix}}}\left(\frac{1}{m_{\text{mix}}} - \frac{1}{2}\right)\right\} \qquad (16)$$

For pure hard-sphere chains ($\beta = 0$ and $\gamma = 0$), eq 16 becomes

$$\frac{B_2^{\text{pure}}}{m^2\sigma^3} = \frac{\pi}{6}\left\{\frac{3}{2} + \frac{5}{2m} + \frac{\alpha}{c}\left(\frac{1}{m} - \frac{1}{2}\right)\right\} \qquad (17)$$

3. Application of the STPT-D Equation of State to Mixtures

3.1. Comparison with Molecular Simulation Data. The compressibility factors of hard-sphere chains of several different lengths have been obtained from molecular simulation.[8,19,20] In contrast, there is relatively little molecular simulation data for mixtures of hard-sphere chains. Honnell and Hall[21] reported the compressibility factors for 8-mer/1-mer and 8-mer/4-mer mixtures. Wichert and Hall[22] examined the compressibility of 4-mer/1-mer and 8-mer/1-mer mixtures with different hard-sphere segment diameters. Recently, Chang and Sandler[23] simulated the compressibility of mixtures of chains containing up to 8 hard-sphere segments. The compressibility factors predicted by eq 13 are compared with some of these data in Figure 1. The average absolute deviation (AAD) between theory and all the available data are summarized in Table 1.

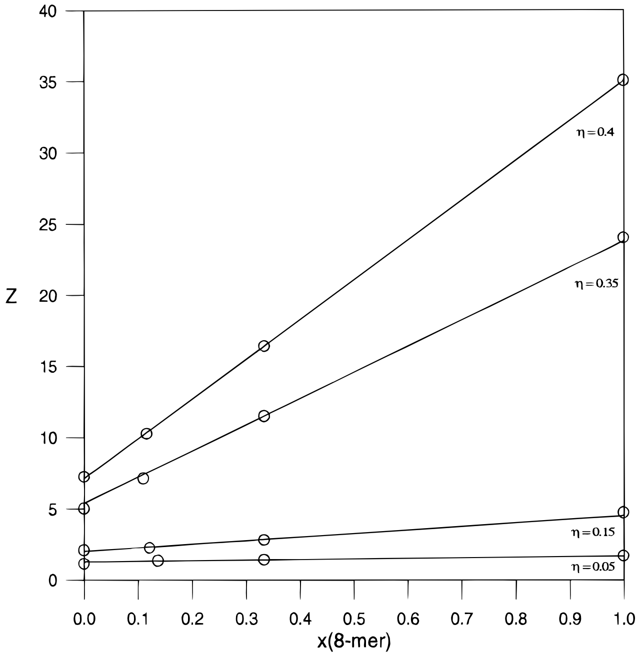

Figure 2. Comparison of the compressibility factor predicted by eq 13 (—) with simulation data[9,21,23,24] (○) at different packing fractions for an 8-mer/1-mer mixture with equal hard-sphere diameters.

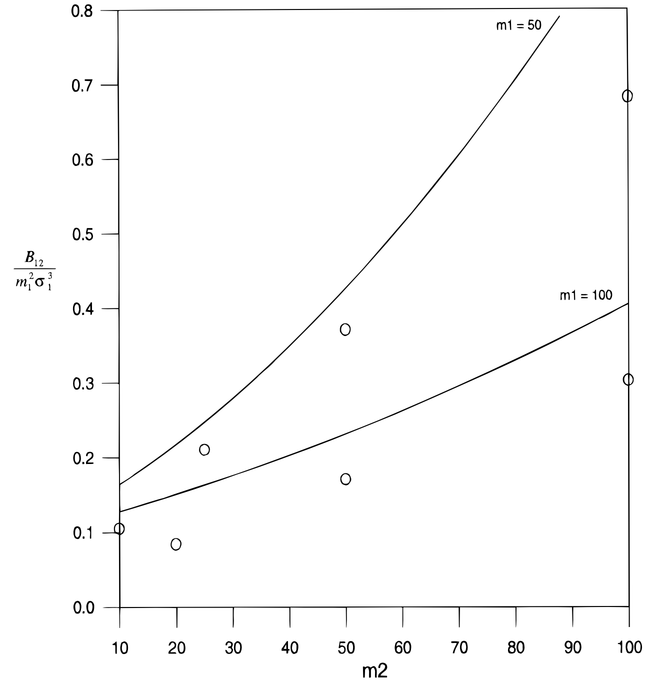

Figure 3. Comparison of the second virial coefficients predicted by eq 16 (—) with simulation data[25] (○) for pairs of hard-sphere chains of equal segment diameters.

$$\text{AAD} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{Z_{i,\text{sim}} - Z_{i,\text{theory}}}{Z_{i,\text{sim}}}\right| \qquad (18)$$

The data in Table 1 indicate that the compressibility factor for the majority of mixtures can be predicted to within an accuracy of ≤5%. Exceptions to this generally good agreement are systems containing hard-sphere segments with substantially different diameters (mixtures 5, 12, and 13). For these mixtures, the inadequate agreement between theory and simulation at high packing fractions makes a large contribution to the overall AADs. Equation 13 is accurate for $\sigma_2/\sigma_1 < 2$.

Table 1. Percentage Average Absolute Deviations (AAD) of the Compressibility Factor Predicted by the STPT-D Equation (Eq 13) Compared with Molecular Simulation Data for Various Binary Mixtures Containing Hard-Sphere Chains of Different Lengths and Segment Diameters[a]

					ADD (%)					
mixture	sim ref	m_1	m_2	σ_2/σ_1	GF-D	Chiew	Song	TPT-1	TPT-D	STPT-D
1	23	2	2	0.6	8.36	0.57	4.34	0.24	0.24	0.35
2	22	4	1	0.5						2.10
3	22	4	1	0.6667						5.25
4	22	4	1	2						3.70
5	22	4	1	4						15.46
6	23	4	2	0.6	7.90	1.55	6.19	1.78	0.64	3.50
7	22	8	1	0.5						6.09
8	22	8	1	0.6667						9.51
9	21	8	1	1						2.45
10	23	8	1	1	2.13	1.63	6.30	3.57	1.21	0.61
11	23	8	1	1.25	2.39	1.33	5.51	3.03	0.82	0.71
12	22	8	1	2						11.92
13	22	8	1	4						22.10
14	21	8	4	1						1.79
15	23	8	4	1	2.98	2.58	8.08	5.10	1.79	1.22

[a] A comparison is also made with the results of other equation of state calculations reported in the literature.[23]

Most of the available simulation data for the compressibility factor of hard-sphere chain mixtures are either at equimolar composition or at a very restricted range of composition. Therefore, it is difficult to examine fully the accuracy of eq 13 over the entire composition range. For the 8-mer/1-mer hard-sphere chain mixture, Chang and Sandler[23] and Honnell and Hall[21] determined the compressibility factor at different 8-mer compositions. These data and simulation results[9,24] for the pure 8-mer and hard-sphere fluids are compared in Figure 2 with the predictions of eq 13 at different packing fractions. This limited comparison indicates that we can expect reasonably good agreement between theory and simulation for the entire composition range.

No molecular simulation data are available for the virial coefficients of hard-sphere chain mixtures. However, Dautenhahn and Hall[25] have reported values of B_{12} for some combinations of hard-sphere chains. Values of B_{12} calculated using eq 16 are compared in Figure 3 with simulation data for pairs of hard-sphere chains of equal segment diameters. It is apparent from this comparison that the ability of the STPT-D equation to determine accurately the virial coefficient declines with increasing chain length.

Some limitations of eq 13 and the potential scope for improvement should be noted. The Boublík[14]/Mansoori et al.[15] equation for hard-sphere mixtures assumes that the diameters of the hard spheres are additive. Equation 13 could be extended to cover nonadditive hard spheres by, for example, adopting the approach suggested by Harvey and Prausnitz.[26] There are insufficient simulation data to fully test the accuracy of eq 5. It is reasonable to assume that the accuracy of eq 5 may deteriorate when there is a large difference in length between the component hard-sphere chains. Similarly, simulation data for mixtures might be required to refine the accuracy of the α and *c* parameters.

3.2. Comparison with Other Hard-Sphere Chain Equations of State for Mixtures. Chang and Sandler[23] have compared the accuracy of five different equations of state for some of the systems studied here. The GF-D equation[19] and the equation proposed by Song et al.[4] were the least accurate of the equations studied by Chang and Sandler. Reasonably good agreement between theory and simulation data was reported for Chiew's[3] equation and the TPT1[27] equation, whereas very good results were obtained for the TPT-D[23] equation. These data are compared in Table 1 (mixtures 1, 6, 10, 11, and 15) with our calculations using the STPT-D equation of state. The data in Table 1 indicate that the accuracy of the STPT-D equation of state for these mixtures is generally superior to the GF-D, Song et al., Chiew, and TPT1 equations of state. The error range for the STPT-D equation is 0.35% to 3.50% compared with an error range of 0.24%−1.79% for the TPT-D equation. This is a good outcome in view of the relative simplicity of the STPT-D equation compared with other equations of state. In particular, the extension to mixtures of the STPT-D equation of state is much simpler than the GF-D equation of state for mixtures.

4. Conclusions

The STPT-D equation of state has been extended to mixtures. The result is a relatively simple equation of state that can be used to predict accurately the compressibility factor of hard-sphere chain mixtures for $\sigma_2/\sigma_1 < 2$. No additional equation of state parameters were required to extend the equation of state to mixtures. However, it is conceivable that additional simulation data for the composition dependence of the α and *c* parameters will enable fine tuning of the accuracy of the equation of state.

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