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An Equation of State for the Hard-Sphere Chain Fluid Based on the Thermodynamic Perturbation Theory of Sequential Polymerization[1]

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New equations of state for freely jointed hard-sphere chain fluids are developed. The equations of state are based on the thermodynamic perturbation theory. The new equations of state use the contact values of the radial distribution function (RDF) for monomer–dimer mixtures, which is derived from the multidensity Ornstein–Zernike theory. These RDFs are composed of a monomer reference term, the Carnahan–Starling or the Percus–Yevick expression, and an additional bond contribution. These equations of state are then extended to real fluids. To calculate the phase equilibrium properties of nonassociating chain fluids, a dispersion contribution is added to the repulsive hard-chain reference term. With the new equations of state of chain fluids supplemented with the dispersion term, the vapor pressures and the coexisting densities of several real fluids are calculated.

KEY WORDS: equation of state; hard-sphere chain fluid; integral equation theory; perturbation theory; statistical associating fluid theory; thermodynamic perturbation theory.

1. INTRODUCTION

Equations of state are used in engineering practice to predict the thermodynamic properties of fluids. Numerous studies have been carried out to develop an accurate equation of state for the thermodynamic properties of fluids. In recent years there have been several equations of state developed for hard-sphere chain fluids based on the rigorous off-lattice statistical

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mechanical theory. Accurate knowledge of the thermodynamic properties of the hard-sphere fluids is important since it could serve as a convenient reference system in developing perturbation theory for more realistic model fluids.

Some years ago, Wertheim formulated the thermodynamic perturbation theory (TPT) and the multidensity Ornstein–Zernike (MOZ) integral equation theory for associating fluids [1, 2], and equations of state for hard diatomics [3] and freely jointed hard-sphere chain fluids [4, 5] were developed. Chapman et al. [6, 7] extended Wertheim's TPT theory to mixtures and real fluids, which is referred to as the statistical associating fluid theory (SAFT). Chang and Sandler [8, 9] developed the TPT-D theory for hard chain fluids using the structural information of a dimer fluid as an intermediate reference system. Huang and Radosz [10, 11] have applied SAFT to a variety of real fluids including polymers.

The objective of this work is to derive an equation of state for the freely jointed hard-sphere chain fluid within the framework of the TPT and MOZ theories. The compressibility factor of chain fluids predicted by the new equations of state is compared with Monte Carlo simulation results. Then this equation of state is extended to real fluids.

2. THEORY

We consider a potential model of the form

$$\phi(r, \Omega_1, \Omega_2) = \phi_{\mathrm{R}}(r, \Omega_1, \Omega_2) + \sum_A \sum_B \phi_{AB}(r, \Omega_1, \Omega_2) \tag{1}$$

where ϕ_{R} is the potential of repulsive interactions of the reference fluid, r is the vector between the center of molecule 1 and that of molecule 2, Ω_i denotes the orientation of molecule i, and ϕ_{AB} is the potential of attractive interactions between associating sites.

2.1. Residual Helmholtz Energy

In the TPT theory, the Helmholtz energy of chain fluids is written

$$\frac{A}{NkT} = \frac{A^{\mathrm{ideal}}}{NkT} + \frac{A_{\mathrm{R}}^{\mathrm{mono}}}{NkT} + \frac{A^{\mathrm{chain}}}{Nkt} \tag{2}$$

where N is the total number of chains, T is the temperature, k is Boltzmann's constant, and A^{ideal}, $A_{\mathrm{R}}^{\mathrm{mono}}$, and A^{chain} are the Helmholtz energies of ideal, reference monomer, and chain contributions, respectively.

In the present formulation for the thermodynamic perturbation theory of *sequential* polymerization, we consider a system of mN associating hard spheres that are to form N hard-sphere chains of length m. In the manner of the sequential polymerization, a dimer is formed from two monomers, a trimer is formed from a dimer and a monomer, etc., and a m-mer from a $(m-1)$-mer and a monomer. In the context of the TPT theory, the Helmholtz energy change associated with the kth polymerization step is approximated by $-kT \ln g(k, 1)$, where $g(k, 1)$ is the contact value of the radial distribution function between an end segment of a k-mer and a monomer. Strictly speacking, this free energy change would vary with the composition of all intermediate chains during the polymerization as well as their lengths. For simplicity if we neglect such intricate effects of the composition on $g(k, 1)$, the Helmholtz energy change for the overall polymerization can be written

$$\frac{A^{\text{chain}}}{NkT} = -\ln[g(1, 1)\, g(2, 1)\, g(3, 1) \cdots g(m-2, 1)\, g(m-1, 1)] \tag{3}$$

Further, we assume that $g(k, 1)$ is independent of k for $k \geqslant 2$:

$$g(2, 1) = g(3, 1) = \cdots = g(m-2, 1) = g(m-1, 1) \tag{4}$$

Equation (4) relies on the fact from the MOZ integral equation theory that the segment–segment correlation function at contact depends only on the number of segments bonded to the two segments, not on their locations or chain length [12]. Also, from the simulation study by Kumar et al. [13], it was shown that $g(k, 1)$ is nearly insensitive to k when $k \geqslant 4$ and is nearly the same as $g(2, 1)$ when $k \geqslant 2$.

Then it follows that

$$\frac{A^{\text{chain}}}{NkT} = -\ln g(1, 1) - (m-2) \ln g(2, 1) \tag{5}$$

where $g(1, 1)$ is equal to $g^{\text{M}}(\sigma)$ and $g(2, 1)$ is identified with the correlation function of a monomer–dimer mixture evaluated at the bond length.

Chang and Kim [12] and Chiew [14, 15] obtained the same expressions for the contact values of the correlation functions from the MOZ and PY theory and calculated the correlation functions for the region beyond the hard core from a set of integral equations. The resulting expression for the contact values of the correlation functions of monomer–dimer mixture is written in the following form:

$$g(2, 1) = g^{\text{M}}(\sigma) - \frac{1}{4(1-\eta)} \tag{6}$$

We obtain two expressions for the RDF of monomer–dimer mixtures from the two expressions for the RDF of hard spheres, the Percus–Yevick and the Carnahan–Starling expressions, respectively [16].

$$g_{\mathrm{PY}}^{\mathrm{MD}}(\sigma)=\frac{1+(\eta/2)}{(1-\eta)^2}-\frac{1}{4(1-\eta)} \tag{7}$$

$$g_{\mathrm{CS}}^{\mathrm{MD}}(\sigma)=\frac{1-(\eta/2)}{(1-\eta)^3}-\frac{1}{4(1-\eta)} \tag{8}$$

Substituting Eqs. (7) and (8) into Eq. (5), we obtain new expressions for the Helmothz free energy that account for the chain contribution in the *sequential* polymerization.

$$\frac{A^{\mathrm{chain}}}{NkT}=-\ln g^{\mathrm{M}}(\sigma)-(m-2)\ln g^{\mathrm{MD}}(\sigma) \tag{9}$$

2.2. Equation of State

The compressibility factors are obtained by differentiating the Helmholtz energy with respect to the density. As is the case for the Helmholtz energy, the compressibility factor is written as a sum of separate contributions. For the compressibility factor we have

$$Z=mZ_{\mathrm{HS}}^{\mathrm{mono}}+Z^{\mathrm{chain}} \tag{10}$$

The compressibility factor of a monomer hard-sphere fluid $Z_{\mathrm{HS}}^{\mathrm{mono}}$ is given by the Carnahan–Starling equation of state,

$$Z_{\mathrm{HS}}^{\mathrm{mono}}=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{11}$$

We obtain two equations of state from two expressions for $g^{\mathrm{MD}}(\sigma)$:

$$Z_{\mathrm{TPT-MOZ}}^{\mathrm{model\,1}}=m\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}-\frac{1+\eta-\frac{1}{2}\eta^2}{(1-\eta)(1-\frac{1}{2}\eta)}-(m-2)\frac{\eta(3+\eta)}{(1-\eta)(\eta+1)} \tag{12}$$

$$Z_{\mathrm{TPT-MOZ}}^{\mathrm{model\,2}}=m\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}-\frac{1+\eta-\frac{1}{2}\eta^2}{(1-\eta)(1-\frac{1}{2}\eta)}-(m-2)\frac{\eta(\eta^2+2\eta-9)}{(1-\eta)(\eta^2-3)} \tag{13}$$

where models 1 and 2 correspond to Eqs. (7) and (8), respectively. These new equations of state for hard-sphere chain fluids are referred to as TPT–MOZ equations in the following discussion.

3. APPLICATION TO REAL FLUIDS

3.1. Dispersion Contribution

To calculate the phase equilibrium properties of nonassociating chain fluids, a dispersion contribution is added to the repulsive hard-chain reference term ($Z_{\text{TPT–MOZ}}^{\text{model 2}}$). The dispersion term is a power series initially fitted by Alder et al., and universal parameters used in this work have been refitted to accurate thermophysical properties for argon by Chen and Kreglewski [17]

3.2. Molecular Parameters

For nonassociating chain molecules, there are three molecular parameters, segment number (m), segment volume (v^{00}), and segment–segment interaction energy (u^{0}), to be determined in these equations of state for pure fluids [10, 11]. Molecular parameters are determined by fitting density and vapor pressure data for liquids and pressure–volume data for gases at a constant temperature.

4. RESULTS AND DISCUSSION

We compare the simulation results for the compressibility factor for hard-sphere chain fluids with the predictions of TPT, TPT-D, and the two models [Eqs. (12) and (13)] developed in this work. The average relative errors for the compressibility factor are listed in Table I. The simulation results of Chang and Sandler [8] and those of Escobedo and de Pablo [18] are used for comparison. As the chain length increases, the discrepancy between the predictions of the theories and simulation data becomes larger. Figure 1 shows the compressibility factor for hard-sphere chain fluids of

Table I. Comparison of the Compressibility Factors of Hard-Sphere Chain Fluids from Various Theories

	AAD (%)[a]			
	TPT	TPT-D	Model 1	Model 2
16-mer	9.1185	2.7750	6.9690	2.4113
32-mer	9.2377	3.1757	8.0590	2.1834

[a] $\text{AAD}(\%) = \sum \left|\frac{\text{simulation} - \text{prediction}}{\text{simulation}}\right| \times 100.$

16- and 32-mers. For the 16-mer fluid, all theories are satisfactory, although the TPT theory overestimates the simulation results at low densities and Model 1 slightly overestimates the simulation results at intermediate and high densities. The overestimations from Model 1 are because of the underestimation of the RDF. The difference between the TPT-D model and Model 2 is very small for the 16-mer fluids, All theories are reasonably accurate, in particular, TPT-D and Model 2. The TPT-D and Model 2 can reproduce the MC results within 3%, Model 1 within about 7%, and TPT within about 9%.

In Fig. 1 predictions of the theories and simulation results for the compressibility factors of the hard-sphere fluids of 32-mers are also compared. Figure 1 shows the same rank for the accuracy of the theories for the compressibility factors as is found for shorter chain fluids. All theories overestimate the compressibility factor, in particular, TPT and Model 1. Model 2 reproduces the simulation results of the compressibility factors of 32-mer fluids to within about 2%, TPT-D about 3%, Model 1 about 8%, and TPT about 9%. The above comparison of the compressibility factors of hard chain fluids by various theories indicates that Model 1

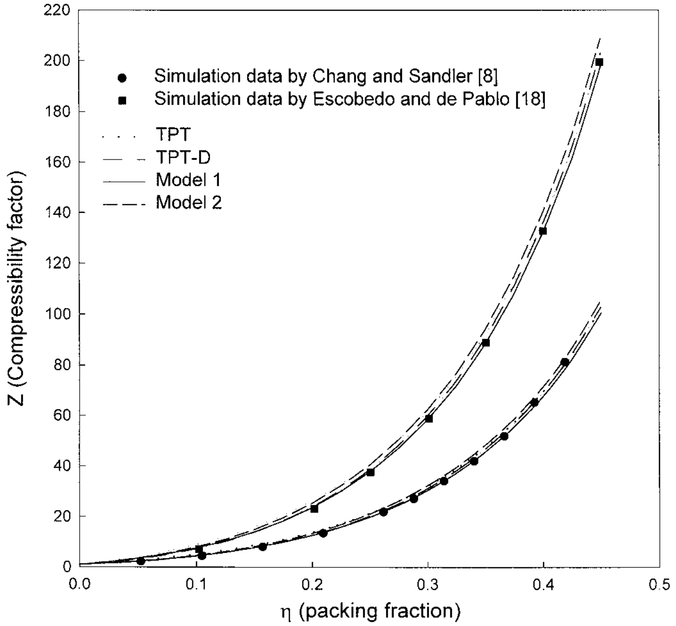

Fig. 1. The compressibility factor of hard-sphere 16- and 32-mer fluids. The symbols are the MC simulation data of Chang and Sandler [8] and Escobedo and Pablo [18], and the lines are from the theories.

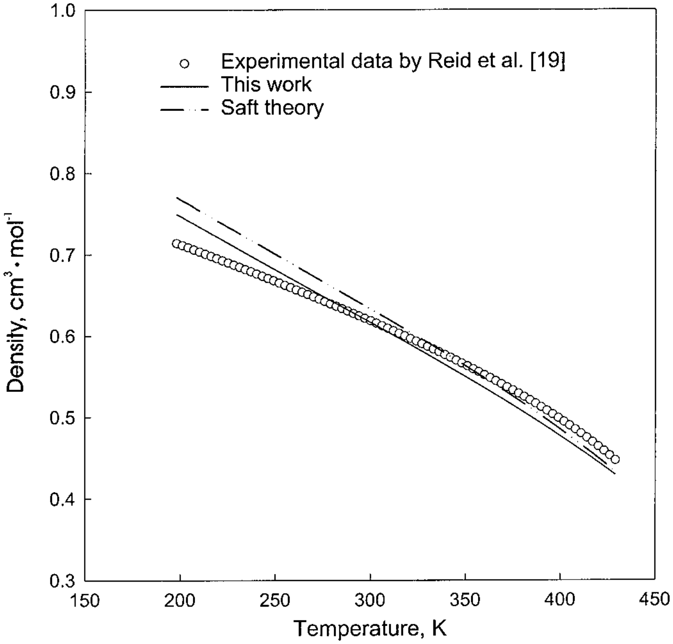

Fig. 2. Predicted liquid densities of pentane. The symbols are the experimental data [19], and the lines are from the theories.

is of nearly the same accuracy as the TPT theory, and Model 2 is comparable to or slightly better than the TPT-D theory. With the new equation of state of chain fluids supplemented with the dispersion term, the vapor pressures and the coexisting densities of several real fluids are calculated. In Figs. 2 and 3 the predictions of the theories are compared with experimental data [19] for the liquid densities of pentane and hexane. For pentane, all theories are satisfactory, although all theories overestimate the experimental data at low temperatures and underestimate them at high temperatures. SAFT can reproduce the experimental data to within about 3%, and our equation to within 3%. For hexane, all theories also overestimate the experimental data at low temperatures and underestimate them at high temperatures. SAFT can reproduce the experimental data to within about 3%, and our equation to within about 2%.

5. CONCLUSIONS

Equations of state for freely jointed hard-sphere chain fluids based on the thermodynamic perturbation theory of sequential polymerization are

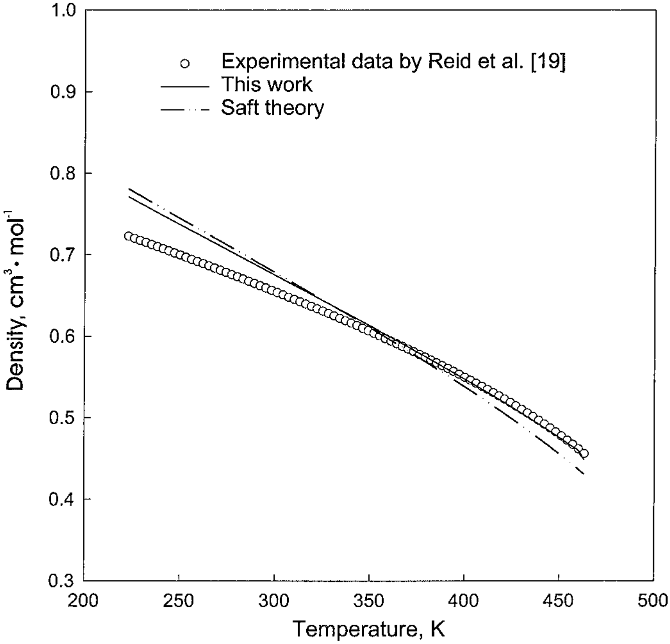

Fig. 3. Predicted liquid densities of hexane. The symbols are the experimental data [19], and the lines are from the theories.

developed. We obtain new expressions for the chain contribution term in the TPT equation of state by using the contact values of the radial distribution function of monomer–dimer mixtures as an intermediate reference system. These expressions for the contact values are adopted from the multidensity Ornstein–Zernike integral equation theory. We obtain equations of states for hard-sphere chain fluids upon using the idea of sequential polymerization and the RDFs of the monomer–dimer mixture. The compressibility factors of chain fluids predicted by the equations of state are compared with MC simulation results, and reasonably good agreement between the theories and simulations is found. We then extend these equations of state to real fluids. To calculate the phase equilibrium properties, the dispersion term is added to the repulsive hard-chain reference term in the Alder et al. equation. With the new equations of state of chain fluids supplemented with the dispersion term, the vapor pressures and coexisting densities of several real fluids are calculated. Again, we find good agreement between the predictions of the theory and the experimental data.

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