

## Equations of State for Hard-Sphere Chains: Effect of Attractive Contribution

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**Abstract:** Several equations of state for hard-sphere chains with various perturbation terms are reviewed. For each model, three characteristic parameters are required to represent phase equilibria of normal fluids and obtained from thermodynamic properties of pure saturated liquids. The models are then compared with computer simulation data to show the effect of attractive contribution forms employed. Calculated values of vapor-liquid equilibria (VLE) of hydrocarbons that can be reproduced for each model are also compared with experimental results. An additional parameter,  $\zeta_{KB}$ , is required to represent the VLE of pure water, which is ascertained to have a strong influence on the theoretical coexistence curve.

**Keywords:** equation of state; hard-sphere chain; attractive contribution.

### Introduction

Equation of state serves as a very efficient tool to describe properties of various kinds of fluids. In recent years, there have been increasing interests in developing equations of state that can describe properties of molecular fluids more accurately and the application of equation of state for the calculation of phase equilibria has been the subject of numerous studies.<sup>1-3</sup> Especially for polyatomic molecules, however, it is very difficult to establish a statistical-mechanical model because of their several distinctions from normal fluids such as asymmetric structure, large number of internal degrees of freedom, and strong coupling between intra- and intermolecular interactions.<sup>4</sup> Among several categories of equation of state, the hard-sphere equation of state is adapted as a very useful reference system to represent numerous types of molecular fluids despite of its simplicity. Further, the hard-sphere system has another merit that it can be extended directly to the hard-sphere-chain system by introducing chain connectivity term, which is used in most existing equations of state for chain-like molecules. A hard-sphere-chain equation of state takes into account some significant features of real fluids including polymers. Based on these approaches, a lot of perturbation theories have been proposed.

To explain the interactions between real fluids, the free energy is expanded in a power series in reciprocal temperature. The first and second-order perturbation terms can be generally calculated using perturbation theory, e.g., Barker-Henderson theory.<sup>5</sup> Depending on the number of perturbation

terms considered, first-order perturbation theories,<sup>6</sup> second-order perturbation theories,<sup>7-9</sup> and fourth-order perturbation theories<sup>10,11</sup> were independently developed. Another simple approach is using a van der Waals perturbation term containing temperature-dependent attractive parameter,  $a(T)$ . It can be related to the second virial coefficient  $B(T)$  and therefore can be determined from the knowledge of intermolecular potential,<sup>12,13</sup> or can be employed simply using empirical temperature dependent functions obtained by fitting the experimental data for several simple fluids such as argon and methane.<sup>14-16</sup>

It has been apprehended that the formation of hard-sphere chain reduces the number of intermolecular interactions when compared to a system of spherical molecules only, which is caused by the shielding of chain segments by other segments of the same chain. This phenomenon is considered to be dependent both on the chain length and the system density. Recently, a number of studies have been reported that account for the connectivity of the segments in the perturbation term. Most of the models are developed in analytical form and shows high accuracy, however, the obtained expressions are too lengthy and difficult to handle.<sup>7,17-26</sup>

In this study, we developed three hard-sphere-chain equations of state based on the well-known Carnahan-Starling hard-sphere equation<sup>27</sup> differing in the perturbation terms, that have more simplified form than those of the models mentioned above. Each model is directly extended from the Carnahan-Starling equation by introducing a bonding term which accounts for the chain connectivity. We then compared each model with computer simulation data and experimental vapor-liquid equilibrium data of pure saturated fluids.

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## Model Descriptions

**Reference Terms.** The equation of state for hard spheres and hard-sphere chains generally consists of two contributions

$$Z = Z_{ref} + Z_{pert} \quad (1)$$

In this study, we employ the well-known Carnahan-Starling (C-S) equation of state<sup>27</sup> as the reference equation for hard spheres.

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

where  $\eta$  is defined as the packing fraction or reduced density which can be expressed as

$$\eta = \frac{\pi\sigma^3}{6}\rho \quad (3)$$

$\sigma$  is the hard-sphere diameter and  $\rho = N/V$  is the number density.

For hard-sphere chains, the hard-sphere equation can be directly extended to the hard-sphere chains by introducing appropriate chain connectivity term. In recent publications, two different types of bonding terms are found and adapted for this study.

$$Z_1^{chain} = (1-r)[g(d^+) - 1] \quad (4)$$

$$Z_2^{chain} = (1-r)\rho \frac{\partial \ln g(d^+)}{\partial \rho} \quad (5)$$

where  $g(d^+)$  is the pair radial distribution function for hard sphere chains at contact:

$$g(d^+) = \frac{1 - 0.5\eta}{(1 - \eta)^3} \quad (6)$$

$$\rho \frac{\partial \ln g(d^+)}{\partial \rho} = \frac{\eta(5 - 2\eta)}{(2 - \eta)(1 - \eta)} \quad (7)$$

Above two equations were compared using the same hard-sphere reference equation.<sup>28</sup> Results show that using eq. (5) describes the computer simulation data for the compressibility factor with higher accuracy than eq. (4), especially for longer chains. Therefore, we employ eq. (5) to generate the equations for the hard-sphere chains from C-S equation by the following relationship proposed by Kim and Bae.<sup>28</sup>

$$Z^{HSC} = 1 + r(Z^{CS} - 1) + Z^{chain} \quad (8)$$

where  $Z^{HSC}$  stands for the reference equation representing the compressibility factor for hard sphere chains,  $Z^{chain}$  is the bonding term which accounts for chain connectivity, and  $Z^{CS}$  represents the C-S hard-sphere equation of state.

The final expression for the reference equation hard-sphere

chain has the form of

$$Z_{ref} = 1 + r \left( \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - 1 \right) + (1 - r)\rho \frac{\partial \ln g}{\partial \rho} \quad (9)$$

### Perturbation Terms.

**Simplest Type of van der Waals Attractive Term:** In 1873, van der Waals proposed the well-known equation of state for normal fluids<sup>29</sup>

$$\frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RTv} \quad (10)$$

where  $P$  is the pressure,  $T$  is the absolute temperature,  $v$  is the molar volume, and  $R$  is the universal gas constant. In the right-hand side of the above equation, the second term represents the attractive forces between two molecules that is inherited from parameter  $a$ . Song *et al.* adapted this perturbation term and proposed the perturbed hard-sphere-chain (PHSC) equation of state to describe the phase equilibrium properties of fluids including chain-like molecules.<sup>14-16</sup>

$$Z_{pert} = -\frac{r^2 a \rho}{kT} \quad (11)$$

The PHSC theory has three characteristic parameters;  $r$  is the number of segments (effective hard spheres) per molecule,  $\sigma$  is the separation distance between segment centers, and  $\varepsilon$  is the segment-pair interaction energy. For hard spheres ( $r=1$ ), eq. (10) reduces to the van der Waals attractive term in eq. (9). In eq. (10), parameter  $a$  which reflects the attractive forces between two non-bonded segments, is temperature-dependent function given by

$$a(T) = \frac{2\pi}{3} \sigma^3 \varepsilon F_a(kT/\varepsilon) \quad (12)$$

where

$$F_a(kT/\varepsilon) = 1.8681 \exp[-0.0619(kT/\varepsilon)] + 0.6715 \exp[-1.7317(kT/\varepsilon)^{3/2}] \quad (13)$$

**Perturbation Term Proposed by Bokis *et al.*:** The PHSC equation proposed by Song *et al.* describes various kinds of thermodynamic properties of fluids and fluid mixtures containing polymeric liquids as well. However, the PHSC equation of state is poor in representing the attractive contributions because it employed the simplest type of van der Waals attractive form as the perturbation term. Bokis *et al.* pointed out this shortcoming that frequently occurs in most of existing equations of state.<sup>6</sup> Simultaneously, they suggested a simple expression for the perturbation term by directly correlating the Monte Carlo simulation data.

$$Z_{pert} = (q_a + q_b \eta) Z_{pert}^1 \quad (14)$$

where  $Z_{pert}^1$  is the attractive contribution to the compressibility factor for a spherical molecule (monomer). In this

study,  $Z_{pert}^1$  is obtained from eq. (10) by setting that  $r=1$ . The final form of the perturbation term for the HSC is then given by

$$Z_{pert} = -(q_a + q_b \eta) \frac{a\rho}{kT} \quad (15)$$

$q_a$  and  $q_b$  are constants for each chain and vary approximately linearly with chain length according to

$$q_a = 0.856 + 0.144r \quad (16a)$$

$$q_b = 2.54(r-1) \quad (16b)$$

**Square-Well Based Equation for the Attractive Term:**

In 1998, Sadowski developed a new equation of state for hard-sphere chains that accounts for the chain connectivity in the reference term as well as in the attractive term.<sup>30</sup> On the other hand, the model developed by Bokis *et al.* is purely empirical and parameters do not have physical meanings. Sadowski derived an equation of state using a physically meaningful expression while retaining a simplicity. For spherical fluids ( $r=1$ ), the attractive contribution is described using a simple mean-field expression

$$Z_{pert}^1 = -\frac{a(T)\rho}{kT} \quad (17)$$

The attraction parameters  $a(T)$  is related to the second virial coefficient  $B(T)$  and the van der Waals covolume  $b$  by

$$\frac{a(T)}{kT} = b - B \quad (18)$$

with  $b(T) = (2\pi/3)\sigma^3$  and  $B = (2\pi/3)\sigma_0^3 [1 + (\lambda^3 - 1)[1 - \exp(-u_0/kT)(1 + 1/T)]]$ .

In this model, the hard-sphere diameter  $\sigma$  is considered as a function of temperature following the Barker-Henderson theory<sup>5</sup>:

$$\sigma = \sigma_0 [1 - C \exp(-3u_0/kT)] \quad (19)$$

with  $C = 0.25$ .

For chain fluids, the compressibility factor of a chain fluid in the attraction term is calculated from that of a spherical fluid using the following relation

$$Z_{pert} = N_{r-r} Z_{pert}^1 \quad (20)$$

where  $N_{r-r}$  is the number of segment-segment interactions in the chain system. For a system which consists of spherical molecules only,  $N_{r-r} = N_{1-1}$  can be calculated as below

$$N_{1-1} = {}_2rC_2 = \frac{(2r)!}{2!(2r-2)!} = r(2r-1) \quad (21)$$

To estimate the number of interactions for the chain system, the ratio of  $N_{r-r} = N_{1-1}$  is approximated to be equal to the ratio of the radial distribution function:

$$\frac{N_{r-r}}{N_{1-1}} = \frac{g_r(\sigma^+)}{g_1(\sigma^+)} \quad (22)$$

The value  $g_1(\sigma^+)$  for the system of hard-spheres can be obtained from the Percus-Yevick equation<sup>12</sup>

$$g_1(\sigma^+) = \frac{2 + \eta}{2(1 - \eta)^3} \quad (23)$$

For hard-sphere chains, Chiew developed an analytical expression for the radial distribution function<sup>31</sup>:

$$g_r(\sigma^+) = \frac{2 + (3r-2)\eta}{2r(1 - \eta)^3} \quad (24)$$

Eq. (24) reduces to eq. (23) for the hard-sphere system ( $r=1$ ).

Using eq. (21) through eq. (24), a number of interactions in the chain system are now determined as:

$$N_{r-r} = \frac{Z_{pert}}{Z_{pert}^1} = (2r-1) \frac{2 + (3r-2)\eta}{2 + \eta} \quad (25)$$

Eq. (25) represents that  $N_{r-r}$  depends on both the segment number and the system density.

For comparison, complete equations of state with three different perturbation terms are given in Table I.

**Thermodynamic Functions.**

**Helmholtz Energy:** The general equation for calculating the Helmholtz energy from a pressure-explicit equation of state is

**Table I. The Proposed Equations of State for Hard Sphere Chains and Their Expressions**

| Equation         | Expression  |
|------------------|---|
| Song's Model     | $Z = 1 + r \left( \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - 1 \right) + (1 - r) \rho \frac{\partial \ln g}{\partial \rho} - \frac{r^2 a \rho}{kT}$ (26)   |
| Bokis' Model     | $Z = 1 + r \left( \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - 1 \right) + (1 - r) \rho \frac{\partial \ln g}{\partial \rho} - (q_a + q_b \eta) \frac{a \rho}{kT}$ (27)  |
| Sadowski's Model | $Z = 1 + r \left( \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} - 1 \right) + (1 - r) \rho \frac{\partial \ln g}{\partial \rho} - (2r - 1) \frac{2 + (3r - 2)\eta}{2 + \eta} \frac{a(T)}{kT} \frac{4\eta}{rb}$ (28) |

$$A(T, V, N_i) = \sum_i^m A_i^0(T) + \int_V \left( P - \frac{Nk_B T}{V} \right) dV + k_B T \sum_i^m N_i \ln \left( \frac{Nk_B T}{V} \right) \quad (29)$$

By introducing eq. (26) into eq. (29), one can obtain the following equation:

$$\frac{\Delta A}{N, kT} = b \rho_r W - \frac{a \rho_r}{kT} - \left( 1 - \frac{1}{r} \right) Q + \frac{1}{r} \ln \left( \frac{1}{r} \rho_r kT \right) \quad (30)$$

In a similar way, the Helmholtz energy for the eqs.(27) and (28) can also be calculated as follows

$$\begin{aligned} \frac{\Delta A}{N, kT} &= \frac{\eta(4-3\eta)}{(1-\eta)^2} + \left( 1 - \frac{1}{r} \right) [3 \ln(1-\eta) - \ln(2-\eta) + \ln 2] \\ &- \frac{4}{r^2} \left( \frac{\varepsilon}{kT} \right) \frac{F_a}{F_b} [(0.856 + 0.144r)\eta + 1.27(r-1)\eta^2] \\ &+ \frac{1}{r} \ln \left( \frac{1}{r} \rho_r kT \right) \end{aligned} \quad (31)$$

and

$$\begin{aligned} \frac{\Delta A}{N, kT} &= 4\eta W - \left( 1 - \frac{1}{r} \right) Q + \frac{1}{r} \ln \left( \frac{1}{r} \rho_r kT \right) \\ &- \left( 2 - \frac{1}{r} \right) \left( \frac{a}{kT} \right) \left( \frac{4}{rb} \right) \left[ 6(1-r) \ln \frac{\eta+2}{2} - (3r-2)\eta \right] \end{aligned} \quad (32)$$

where

$$W = \frac{(4-3\eta)}{4(1-\eta)^2} \quad (33)$$

$$Q = \ln \frac{2-\eta}{2(1-\eta)^3} \quad (34)$$

**Chemical Potential:** The chemical potential is given by

$$\mu_k = \left( \frac{\partial A}{\partial N_k} \right)_{T, V, N_{i \neq k}} \quad (35)$$

or

$$\frac{\mu_k}{kT} = r \frac{\partial}{\partial \eta} \left( \eta \frac{\Delta A}{N, kT} \right)_{T, V, N_{i \neq k}} \quad (36)$$

By differentiating eqs. (30) through (32) with respect to the number of molecules in the system, the expressions for the chemical potential for each model can be obtained:

$$\begin{aligned} \frac{\Delta \mu_k}{k_B T} &= 8r\eta W + 4r\eta^2 \frac{\partial W}{\partial \eta} - (r-1)Q - (r-1)\eta \frac{\partial Q}{\partial \eta} \\ &- \frac{8r}{b} \left( \frac{a}{kT} \right) \eta + \ln \left( \frac{4kT}{rb} \eta \right) + 1 \end{aligned} \quad (37)$$

$$\begin{aligned} \frac{\Delta \mu_k}{k_B T} &= rM + r\eta \frac{\partial M}{\partial \eta} + (r-1)N + (r-1)\eta \frac{\partial N}{\partial \eta} \\ &- \frac{4}{r} \left( \frac{\varepsilon}{kT} \right) \frac{F_a}{F_b} \left( X + \eta \frac{\partial X}{\partial \eta} \right) + \ln \eta \end{aligned} \quad (38)$$

$$\begin{aligned} \frac{\Delta \mu_k}{k_B T} &= 8r\eta W + 4r\eta^2 \frac{\partial W}{\partial \eta} - (r-1)Q - (r-1)\eta \frac{\partial Q}{\partial \eta} \\ &+ \ln \left( \frac{4kT}{rb} \eta \right) - (2r-1) \left( \frac{a}{kT} \right) \left( \frac{4}{rb} \right) \left[ 6(1-r) \ln \frac{\eta+2}{2} \right. \\ &\left. + 2(3r-2)\eta + 6(1-r) \frac{\eta}{\eta+2} \right] + 1 \end{aligned} \quad (39)$$

where

$$M = \frac{\eta(4-3\eta)}{(1-\eta)^2} \quad (40)$$

$$N = \ln \frac{2(1-\eta)^3}{2-\eta} \quad (41)$$

$$X = (0.856 + 0.144r)\eta + 1.27(r-1)\eta^2 \quad (42)$$

**Fugacity Coefficient:** The condition for the vapor-liquid equilibria of pure fluids is given by

$$\Delta \mu^V = \Delta \mu^L \quad (43)$$

$$f^V = f^L \quad (44)$$

where  $f$  is the fugacity and superscripts  $V$  and  $L$  refer to the vapor phase and the liquid phase, respectively.

For a pure component, the fugacity coefficient  $\phi$  can be obtained from the following relationship:

$$\ln \phi = \int_V \left[ \frac{P}{nRT} - \frac{1}{V} \right] dV - \ln Z + (Z-1) \quad (45)$$

Substituting eqs. (26)-(28) into eq. (45) yields

$$\begin{aligned} \ln \phi &= r \left[ \frac{3-2\eta}{(1-\eta)^2} - 3 \right] + (r-1) [3 \ln(1-\eta) - \ln(2-\eta) + \ln 2] \\ &- \frac{4r}{b} \left( \frac{a}{kT} \right) \eta - \ln Z_1 + Z_1 - 1 \end{aligned} \quad (46)$$

$$\ln \phi = rM + (r-1)N - \frac{4}{r} \left( \frac{\varepsilon}{kT} \right) \frac{F_a}{F_b} X - \ln(Z_2) + Z_2 - 1 \quad (47)$$

$$\begin{aligned} \ln \phi &= 4r\eta W - (r-1)Q - \ln Z_3 + (Z_3 - 1) \\ &- (2r-1) \left( \frac{a}{kT} \right) \left( \frac{4}{rb} \right) \left[ 6(1-r) \ln \frac{\eta+2}{2} + (3r-2)\eta \right] \end{aligned} \quad (48)$$

where  $Z_1$ ,  $Z_2$ , and  $Z_3$  correspond to eqs. (26), (27), and (28), respectively.

## Results and Discussion

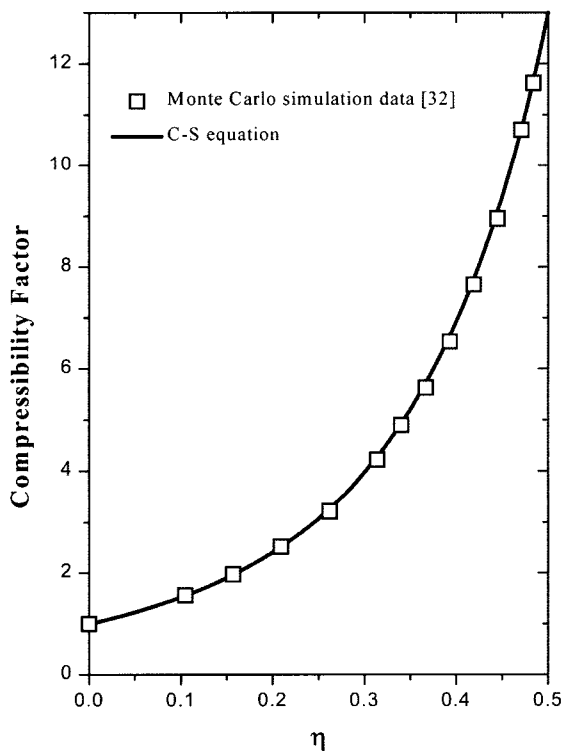
**Compressibility Factor.** The models employed in this work have three characteristic parameters: the number of single hard spheres per chain molecule  $r$ , the segment size  $\sigma$  or  $\sigma_0$ , and the non-bonded segment pair interaction energy  $\varepsilon$  or  $u_0$ .

In Figure 1, Monte Carlo simulation data<sup>32</sup> for the compressibility factor for a spherical molecule are given together with the predicted compressibility factor by the C-S equation. As shown in Figure 1, the calculated values show remarkably good agreement with the simulation data in the entire density region.

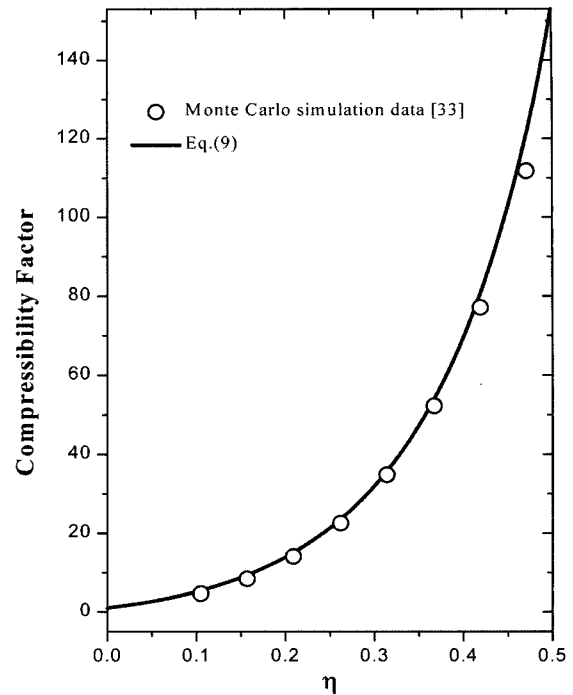
Figure 2 represents a comparison of the compressibility factor from Molecular Dynamics data<sup>33</sup> for pure fluid  $r=16$  with the prediction by eq. (9). In the descriptions of the computer simulation data, the proposed model slightly overestimates the pressure in the higher density region.

Figure 3 compares Monte Carlo simulation data<sup>34</sup> for the compressibility factor of binary hard-sphere chain mixture with the values calculated by eq. (9) ( $\sigma_1/\sigma_2=4/1$ ;  $r_1/r_2=1/16$ ;  $x_1=0.2$ ). It is apparent from the figure that the proposed model describes the simulation data with high accuracy.

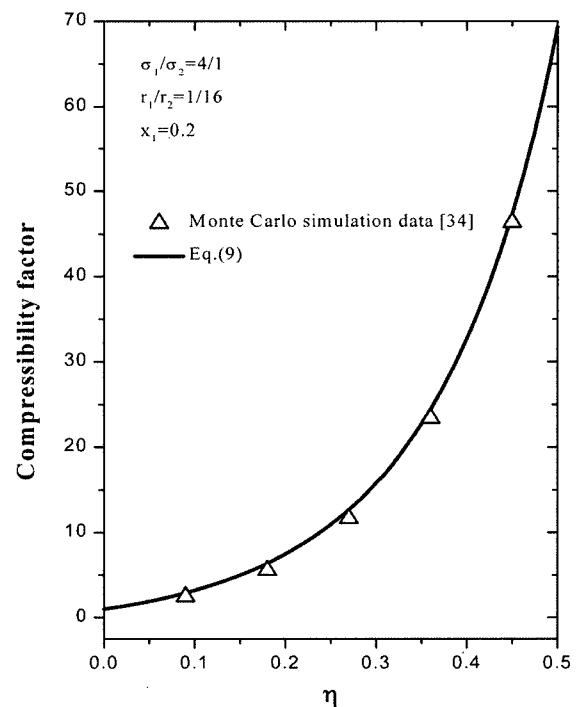
**Attractive Contribution to the Compressibility Factor.** We investigate the attractive contributions to the compress-



**Figure 1.** Monte Carlo simulation data for the system of spherical molecule ( $r=1$ ) which represents the compressibility factor. The solid line is calculated by the C-S equation. The open squares are simulation data reported by Barker and Henderson.<sup>32</sup>



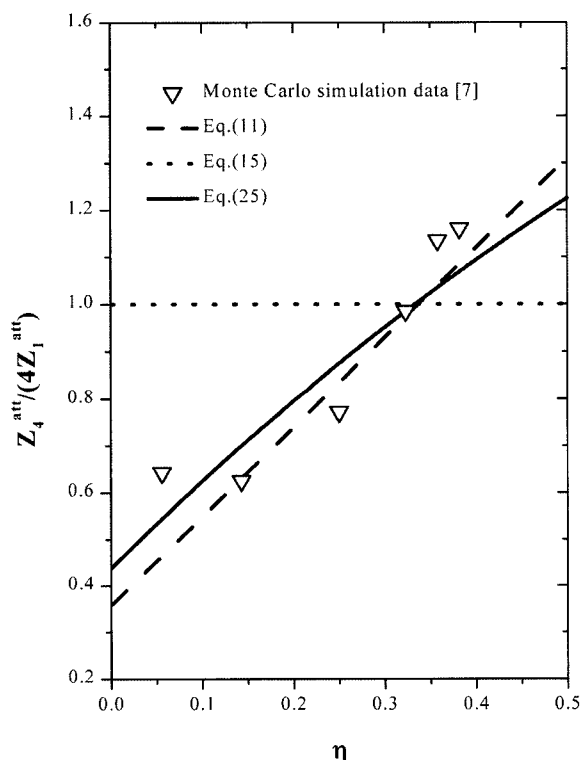
**Figure 2.** Molecular Dynamics data for the system of which effective chain length is 16 which represents the compressibility factor. The solid line is calculated by eq. (9). The open circles are dynamics data reported by Gao and Weiner.<sup>33</sup>



**Figure 3.** Monte Carlo simulation data for the system of mixture of hard sphere chains with  $x_1=0.2$ ,  $r_1/r_2=1/16$ , and  $\sigma_1/\sigma_2=4/1$  which represent the compressibility factor. The solid line is calculated by eq. (9). The open up-triangles are simulation data reported by Dickman and Hall.<sup>34</sup>

ibility factor separately to illustrate the effect of perturbation terms on the overall equation of state. Each contribution is compared with the computer simulation data. The results are shown in Figure 4. This figure represents the ratio of attractive compressibility factor of 4-mer to that of spherical molecule versus the reduced density. The symbols are computer simulation data reported by Yethiraj and Hall.<sup>7</sup> The lines are predictions from each model as denoted in the figure. In Figure 4, eq. (11) reflects no density dependence, keeping the value of  $Z_{pert}^A/(4Z_{pert}^1)$  to be a unity where  $Z_{pert}^A$  represents a contribution of the perturbation term to the compressibility factor of a chain composed of  $r$  hard spheres, while the values  $Z_{pert}^A/(4Z_{pert}^1)$  of calculated from eqs. (15) and (25) increase with density. However, eq. (15) is derived by directly fitting the molecular simulation data with physically insignificant parameters and also the calculated values of  $Z_{pert}^A/(4Z_{pert}^1)$  increase linearly with the hard-sphere density. Eq. (28) is obtained by assuming that the ratio of the number of segment-segment interactions in the chain system is equal to the ratio of the radial distribution function. As shown in Figure 4,  $Z_{pert}^A/(4Z_{pert}^1)$  calculated from eq. (28) fairly agrees with the simulation data without any fitting parameters, and these values increase with the system density.

**Vapor-Liquid Equilibria of Normal Hydrocarbons.** To describe the vapor-liquid equilibria of pure fluids, three tem-



**Figure 4.** Ratio of the attractive compressibility factor of 4-mer to that of monomer versus the reduced density. The lines are calculated by each model as denoted in the figure. The open downward triangles are Monte Carlo simulation data by Yethiraj and Hall.<sup>7</sup>

perature-dependent characteristic parameters ( $r$ ,  $\sigma$ ,  $\epsilon$ ) are required that are obtained appropriately for each model. Those are determined by fitting experimental properties of the pure saturated liquid such as a vapor pressure and a density as a function of temperature. Values for these characteristic parameters of some pure volatile fluids for each model are listed in Tables II-IV.

In Figure 5, presented models are compared with experimental vapor-liquid equilibrium data for saturated pure

**Table II. Lists of Characteristic Parameters for the Song's Equation of State**

| Fluids          | $r$   | $\sigma$ (Å) | $\epsilon/k$ (T) |
|-----------------|-------|--------------|------------------|
| Methane         | 1     | 4.073        | 174.7            |
| Ethane          | 1.757 | 3.748        | 204.5            |
| Propane         | 2.142 | 3.810        | 223.4            |
| Butane          | 2.977 | 3.583        | 211.7            |
| Hexane          | 4.782 | 3.332        | 197.9            |
| Isobutane       | 3.102 | 3.456        | 196.4            |
| Cyclohexane     | 3.689 | 3.434        | 248.5            |
| Ethene          | 1.625 | 3.709        | 198.5            |
| Propene         | 2.173 | 3.689        | 217.6            |
| cis-1-Butene    | 3.148 | 3.452        | 210.6            |
| Benzene         | 3.558 | 3.197        | 263.1            |
| o-Xylene        | 4.461 | 3.369        | 283.0            |
| Acetone         | 3.578 | 3.006        | 245.1            |
| Methyl Chloride | 2.388 | 3.121        | 247.6            |

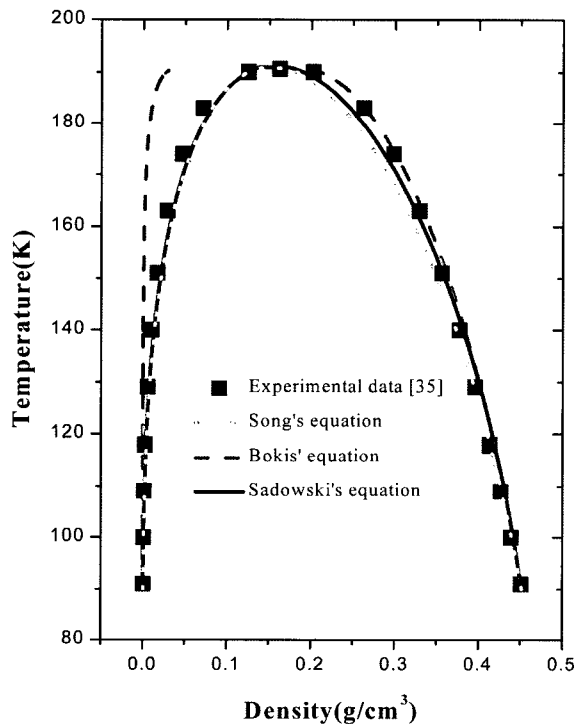
**Table III. Lists of Characteristic Parameters for The Bokis' Equation of State**

| Fluids          | $r$   | $\sigma$ (Å) | $\epsilon/k$ (T) |
|-----------------|-------|--------------|------------------|
| Methane         | 1.198 | 4.078        | 133.8            |
| Ethane          | 1.624 | 3.996        | 262.1            |
| Propane         | 2.363 | 3.819        | 446.3            |
| Butane          | 2.351 | 4.121        | 511.8            |
| Hexane          | 3.582 | 3.924        | 933.4            |
| Isobutane       | 2.583 | 3.981        | 536.5            |
| Cyclohexane     | 3.356 | 3.820        | 947.6            |
| Ethene          | 1.576 | 3.950        | 242.6            |
| Propene         | 2.154 | 3.852        | 404.2            |
| cis-1-Butene    | 2.813 | 3.714        | 624.4            |
| Benzene         | 3.029 | 3.723        | 865.0            |
| o-Xylene        | 3.695 | 3.848        | 1195.4           |
| Acetone         | 2.894 | 3.519        | 747.9            |
| Methyl Chloride | 2.475 | 3.282        | 523.8            |

**Table IV. Lists of Characteristic Parameters for the Sadowski's Equation of State**

| Fluids          | $r/M$   | $\sigma_0$ (Å) | $u_0/k$ (T) |
|-----------------|---------|----------------|-------------|
| Methane         | 0.06814 | 4.024          | 28.152      |
| Ethane          | 0.05228 | 4.108          | 35.893      |
| Propane         | 0.04386 | 4.289          | 39.511      |
| Butane          | 0.03884 | 4.421          | 42.965      |
| Hexane          | 0.03366 | 4.587          | 48.092      |
| Isobutane       | 0.03738 | 4.502          | 40.382      |
| Cyclohexane     | 0.03212 | 4.415          | 50.637      |
| Ethene          | 0.04985 | 4.204          | 41.495      |
| Propene         | 0.03902 | 4.339          | 41.039      |
| cis-1-Butene    | 0.03710 | 4.201          | 45.210      |
| Benzene         | 0.03409 | 4.167          | 51.323      |
| o-Xylene        | 0.03098 | 4.343          | 54.390      |
| Acetone         | 0.03249 | 4.736          | 59.203      |
| Methyl Chloride | 0.06230 | 4.329          | 33.405      |

methane.<sup>35</sup> As shown in this figure, each model is in good agreement with the data, however, the Bokis' model slightly deviates from the experimental data near the critical point.



**Figure 5.** Vapor-liquid equilibrium experimental data for saturated methane. The lines are calculated by each model as denoted in the figure. The solid squares are experimental data reported by Smith and Srivastava.<sup>35</sup>

The Song's and Sadowski's models show almost identical results.

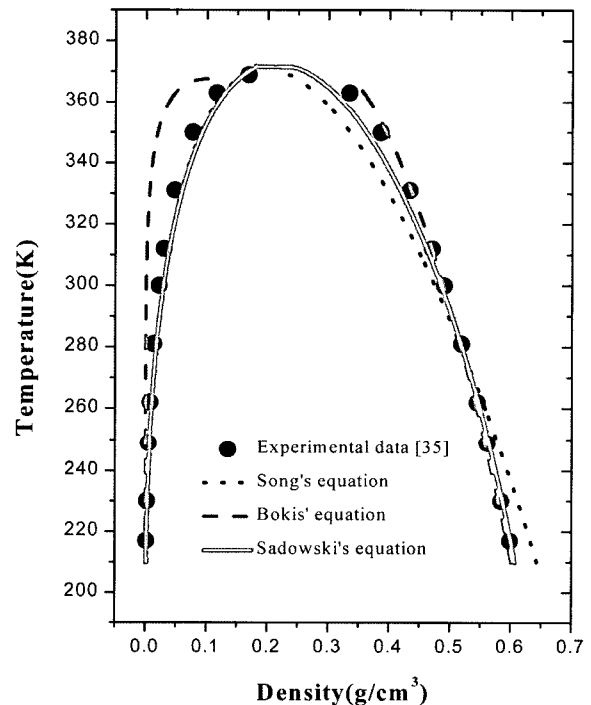
Figures 6 and 7 show results of comparisons of each model with experimental vapor-liquid equilibrium data for propane and hexane.<sup>35</sup> Each model shows similar results to those given in Figure 5. The Bokis' model again shows slight deviations near the critical point in low-density region. The Song's equation also slightly deviates from experimental data and deviations become greater with the molecular weight or the molecular size of the fluids. The Sadowski's model shows similar tendencies to the Song's model, however, best describes vapor-liquid equilibria of pure fluids among presented models.

**Vapor-Liquid Equilibria of Water:** In Figure 8, we present results of comparisons of calculated values from each model with the experimental data of vapor-liquid equilibria of pure water. As shown in the figure, each model shows severe deviations from the experimental data.

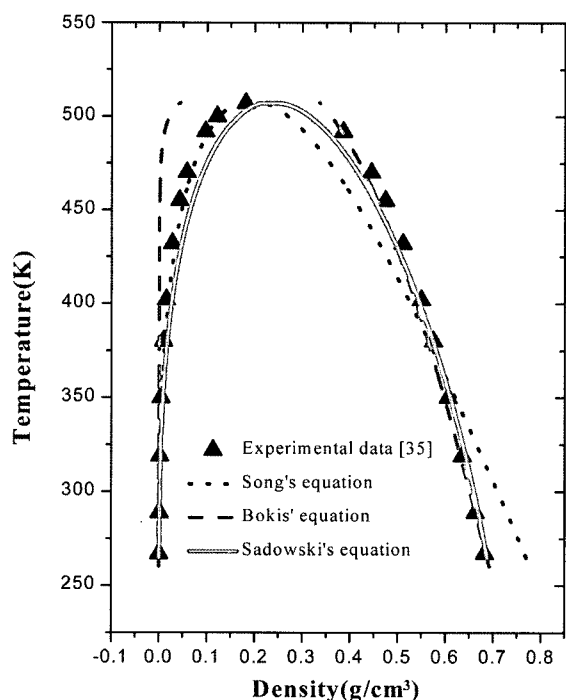
In Sadowski's model, eq. (22) was obtained by a rough approximation. We reconsider Sadowski's equation by proposing the following relationship:

$$\frac{N_{r-r}}{N_{1-1}} \propto \frac{g_r(\sigma^+)}{g_1(\sigma^+)} \quad (49)$$

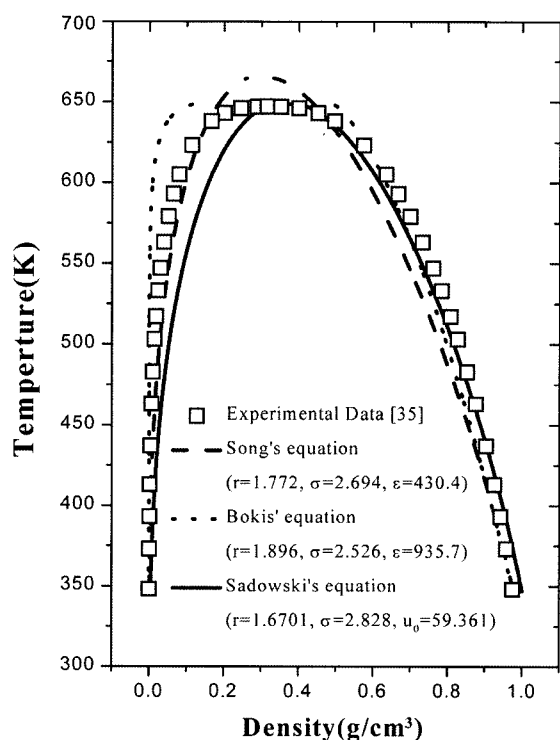
The equality only can be granted by introducing another



**Figure 6.** Vapor-liquid equilibrium experimental data for saturated propane. The lines are calculated by each model as denoted in the figure. The solid circles are experimental data reported by Smith and Srivastava.<sup>35</sup>



**Figure 7.** Vapor-liquid equilibrium experimental data for saturated hexane. The lines are calculated by each model as denoted in the figure. The solid circles are experimental data reported by Smith and Srivastava.<sup>35</sup>



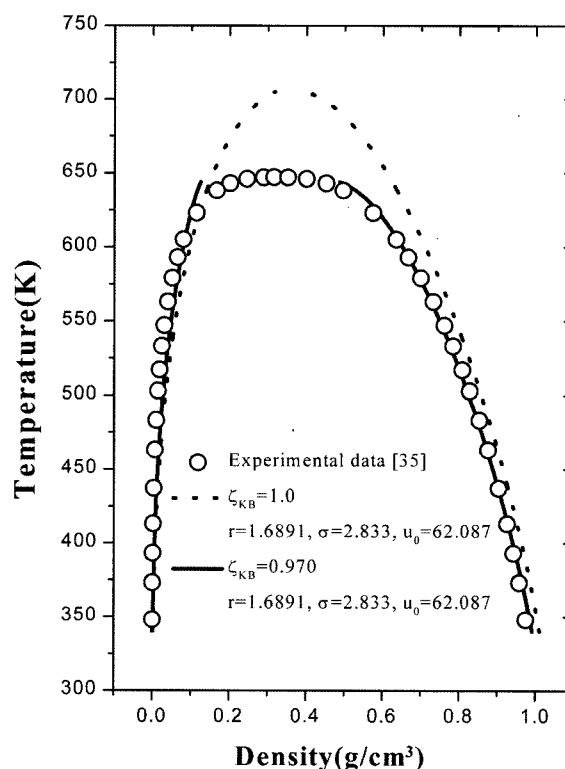
**Figure 8.** Vapor-liquid equilibrium experimental data for saturated water. The lines are calculated by each model as denoted in the figure. The open squares are experimental data reported by Smith and Srivastava.<sup>35</sup>

characteristic parameter,  $\zeta_{KB}$ , which scales the non-ideal behavior of water from normal hydrocarbons. The new expression has the form of

$$\frac{N_{r-r}}{N_{1-1}} = \zeta_{KB} \frac{g_r(\sigma^+)}{g_1(\sigma^+)} \quad (50)$$

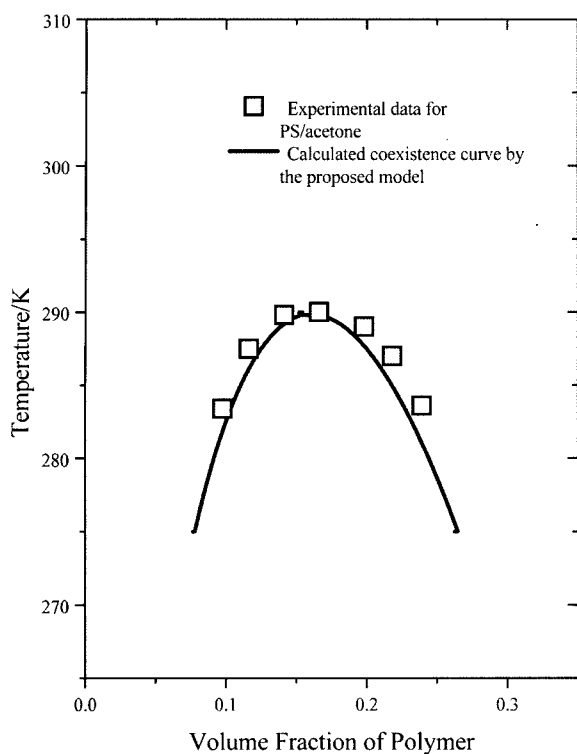
The value of  $\zeta_{KB}$  for pure water is empirically obtained as 0.97. Three characteristic parameters are  $r=1.6891$ ,  $\sigma=2.833$ , and  $u_0=62.087$ . In Figure 9, experimental vapor-liquid equilibria of saturated pure water are compared with theoretical prediction from the modified Sadowski's model. The coexistence curve calculated from the original Sadowski's model with same characteristic parameters is also given for comparison. The result manifests that  $\zeta_{KB}$  strongly influences on the phase diagram of vapor-liquid equilibria for water when the identical characteristic parameters are used. The improved model shows remarkably good agreement with the experimental data.

**Liquid-Liquid Equilibria of Polymer Solutions.** Figure 10 shows cloud point data for binary polystyrene (PS)/acetone system which shows a upper critical solution temperature (UCST) behavior. The open squares are the experimental data reported by Zeman *et al.*<sup>13</sup> and the solid line is calculated



**Figure 9.** Vapor-liquid equilibrium experimental data for saturated water. The lines are calculated by Sadowski's model with different values of  $\zeta_{KB}$  as denoted in the figure. The open circles are experimental data reported by Smith and Srivastava.<sup>35</sup>





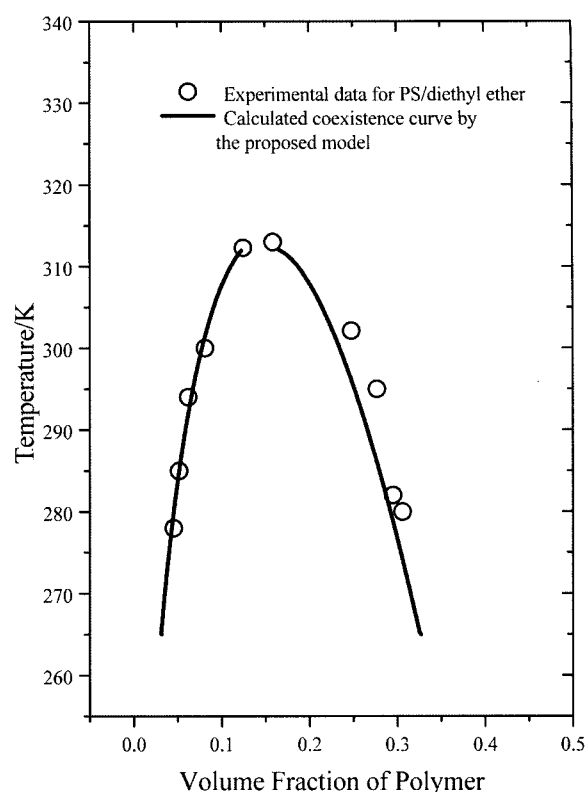
**Figure 10.** Liquid/liquid equilibria for polystyrene/acetone. The solid line is calculated by the proposed model. The open squares are experimental data by Zeman *et al.*<sup>36</sup>

coexistence curve by the proposed model. The values of three characteristic parameters for polystyrene are  $r/M=0.01203$  (mol/g),  $\sigma=5.563\text{\AA}$ , and  $\varepsilon/k=726.8$ . The binary model parameters have the value of  $k_{12}=0.2106$  and  $\lambda_{12}=0.1865$ . From the values of binary model parameters, we can infer that the PHSC equation-of-state theory overestimates  $\varepsilon_{12}$  and  $\sigma_{12}$  by about 21 and 19%, respectively. The calculated coexistence curve shows a slightly narrow values compared with the experimental data. It still predicts the critical point remarkably well.

Figure 11 represents a cloud point curve of the PS/diethyl ether system which shows a UCST behavior. The open circles are the experimental data reported by Zeman *et al.*<sup>13</sup> and the solid line is the calculated coexistence curve by the proposed model. Binary model parameter values for our proposed model are  $k_{12}=0.1845$  and  $\lambda_{12}=0.1558$ . The PHSC equation-of-state theory overestimates the energy and size parameters about 18 and 16%, respectively. The proposed model slightly overestimates the experimental critical point and shows a slight deviation from the experimental data in the higher polymer composition region.

## Conclusions

Three different types of perturbation terms are adapted to the well-known Carnahan-Starling (C-S) hard-sphere equa-



**Figure 11.** Liquid/liquid equilibria for polystyrene/diethyl ether. The solid line is calculated by the proposed model. The open circles are experimental data by Zeman *et al.*<sup>36</sup>

tion of state to calculate thermodynamic properties of various molecular fluids. To extend each model to hard-sphere chains, a bonding term that represents the chain connectivity is required. Three characteristic parameters for each model are determined from experimental data of pure fluids. In comparison with computer simulation data, Bokis' and Sadowski's models show attractive contributions to the compressibility factor fairly well, however, the Song's model cannot represent density dependence of the ratio of attractive compressibility factor of hard-sphere chain to that of spherical molecule when plotted versus the reduced density. Vapor-liquid equilibria of saturated pure fluids is reproducible using three characteristic parameters without any additional adjustable parameters with high accuracy. The Sadowski's model best describes experimental vapor-liquid equilibria of pure hydrocarbons, while the Bokis' model shows deviations in low-density region. To describe vapor-liquid equilibria of saturated pure water that shows a unique behavior, an additional scaling parameter,  $\zeta_{KB}$  is introduced into the Sadowski's model. The improved equation describes the vapor-liquid equilibria of water remarkably well while the original model shows a large deviation from the experimental data. Using characteristic parameters obtained from pure substances, the LLE of the given polymer/solvents systems were predicted. Calculated coexistence curves show good agreements with the experi-

mental data. The proposed model can explain the non-ideal behaviors of polymer solutions by performing a simple modification on the PHSC equation of state.

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