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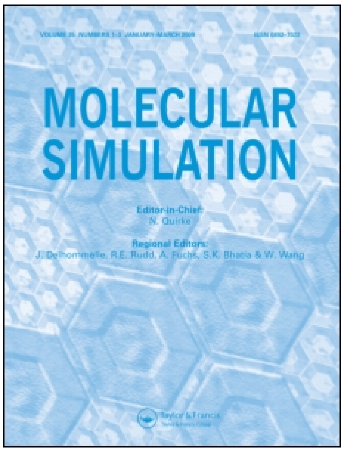

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Renormalization Group Theory Applied for Fluids and Mixtures up to Critical Region

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A simplified equation of state from Statistical Associating Fluid Theory is combined with the Renormalization Group theory to express vapor–liquid equilibria and critical properties of non-polar, polar and associating chain fluids and mixtures over a wide range of state up to the critical region. The results for alkanes, ketones and water from equations of state before and after the RG correction are compared in detail with experimental data from literature. The phase equilibria and critical lines of binary non-polar mixtures are also calculated using a selected mixing rule.

Keywords: Renormalization group theory; SAFT; Phase equilibria; Critical properties

INTRODUCTION

The statistical associating fluid theory (SAFT) proposed by Chapman *et al.* [1] and Huang and Radosz [2] is a theoretically based equation of state (EOS) that has become the most widely used for calculating phase equilibria for a wide variety of complex chain systems. However, its mean-field feature limits its success to the region far from the critical point.

Renormalization group (RG) theory, originally proposed by Wilson [3] for Ising spins and lattice gas, was further modified by White [4,5] for freely moving molecules. Applications of White's RG theory can be found for both square-well (SW) [6], Lennard–Jones (LJ) [7] fluids. Calculation for more complex molecules was also carried out for chain fluids by Jiang and Prausnitz [8]. These applications demonstrate that the theory is capable of grasping global behaviors of fluids.

In this paper, a simplified EOS from SAFT combined with RG theory is established to calculate phase equilibria and critical properties for pure non-polar, polar and associating chain fluids and non-polar binary mixtures. Critical curve of binary mixtures is also discussed.

SIMPLIFIED SAFT EQUATION OF STATE

The Simplified SAFT equation of state is defined in terms of the residual Helmholtz energy density, i.e. the Helmholtz energy per unit of volume, which has the following term:

$$f^{\mathrm{SAFT}} = f^{\mathrm{id}} + f^{\mathrm{hs}} + f^{\mathrm{dis}} + f^{\mathrm{chain}} + f^{\mathrm{dd}}. \tag{1}$$

Compared with the original SAFT, two terms are changed. First, for the dispersion term, the equation of Cotterman *et al.* [9] is adopted, instead of the Alder's term. Second, the dipole–dipole interaction term f^{dd} is given by the equation of Twu and Gubbins [10], and the non-explicit association term in the original SAFT [2] is omitted in the study. For associating fluids, the dipole moment is considered to be dependent on the density with a parameter c, as suggested by Kraska and Gubbins [11]. All terms in Eq. (1) are listed below.

The contribution of the ideal gas is given by:

$$f^{\mathrm{id}} = kT[\rho \ln(\rho \Lambda^3) - \rho]. \tag{2}$$

Here, k is Boltzmann constant, T is the temperature, ρ is the number density of molecules and Λ denotes the de Broglie thermal wavelength.

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The hard-sphere interaction is given by the Carnahan–Starling [12] equation:

$$f^{\mathrm{hs}} = kTm\rho\frac{4\eta - 3\eta^2}{(1-\eta)^2} \tag{3}$$

in which η is the packing fraction defined by $\eta = \frac{\pi}{6}m\rho d^3$. And the repulsive part of potential is approximated as being that for a hard sphere of diameter d given by Cotterman *et al.* [9]:

$$\frac{d}{\sigma} = \frac{1 + 0.2977T^*}{1 + 0.3316T^* + 0.001047T^*} \tag{4}$$

here σ is the segment diameter of the repulsive interaction, T^* is the reduced temperature, $T^* = kT/\epsilon$.

For dispersion term, the result of Cotterman *et al.* [9] is adopted, which was tested by LJ molecular simulation data, as the contribution of dispersion interaction to Helmholtz free energy:

$$f^{\mathrm{dis}} = m\rho\varepsilon\left(a^{\mathrm{dis}}_{0,1} + \frac{a^{\mathrm{dis}}_{0,2}}{T^*}\right) \tag{5}$$

$$a^{\mathrm{dis}}_{0,1} = \rho_\tau\Big(-8.5959 - 4.5424\rho_\tau - 2.1268\rho_\tau^2 + 10.285\rho_\tau^3\Big) \tag{6}$$

$$a^{\mathrm{dis}}_{0,2} = \rho_\tau\Big(-1.9075 + 9.9724\rho_\tau - 22.216\rho_\tau^2 + 15.904\rho_\tau^3\Big) \tag{7}$$

with $\rho_\tau = \frac{6}{\sqrt{2}\pi}\eta$, and ϵ is the LJ dispersion energy parameter.

The chain contribution in Eq. (1) is related to the radial distribution function of the hard-sphere fluid at contact, $g^{\mathrm{hs}}(d)$, as follows

$$f^{\mathrm{chain}} = kT(1-m)\rho\ln g^{\mathrm{hs}}(d) \tag{8}$$

where $g^{\mathrm{hs}}(d) = \frac{1-0.5\eta}{(1-\eta)^3}$

The dipole–dipole interaction term f^{dd} is given by Twu and Gubbins [10]:

$$f^{\mathrm{dd}} = \varepsilon\rho\left(\frac{A_2}{1-(A_3/A_2)}\right) \tag{9}$$

$$A_2 = -\frac{2\pi}{3}\frac{\rho^*\mu^{*4}}{T^*}J^{(6)} \tag{10}$$

$$A_3 = \frac{32\pi^3}{135}\sqrt{\frac{14\pi}{5}}\frac{\rho^{*2}\mu^{*6}}{T^{*2}}K^{333}_{222} \tag{11}$$

here $\mu^* = \mu\sqrt{\varepsilon m d^3}$, $\rho^* = m\rho d^3$, the coefficients $J^{(6)}$ and K^{333}_{222} are integrals over two-body and three-body correlation functions; and μ is the experimentally measured dipole moment on the condition of dilute gas.

For associating chain fluids, the dipole moment is considered to be alterable as suggested by Kraska and Gubbins [11]

$$\mu' = \mu(1 + c\rho^*) \tag{12}$$

where μ is the experimentally measured dipole moment on the condition of dilute gas; c is an adjustable parameter.

Thus, parameters used in the simplified SAFT for non-polar and polar fluids are segment number m, segment interaction parameter ε/k and segment diameter σ. All of them are adjustable as used in the original SAFT. And for associating fluids the dipole moment μ and another adjustable parameter c are added.

For non-polar mixtures, van der Waals one-fluid (vdW1) mixing rules are adopted to obtain parameters of mixtures with Panagiotopoulos and Reid combining rules [13] including k_{ij} and k_{ji} as two binary parameters.

SIMPLIFIED SAFT EQUATION OF STATE WITH CORRECTION BASED ON RENORMALIZATION GROUP THEORY

The general equation for the Helmholtz energy density for a fluid is usually divided into two parts: short-range and long-range contributions. According to the White's RG theory [4,5], a contribution from long-wavelength fluctuations is added to the original SAFT terms for Helmholtz energy density:

$$f_0 = f^{\mathrm{SAFT}} + a\rho^2. \tag{13}$$

The renormalization method of the White [4,5] and approximate recursion of Lue and Praustinz [6] is used:

$$f_n(\rho) = f_{n-1}(\rho) + \delta f_n(\rho) \tag{14}$$

where the increment $\delta f_n(\rho)$ at each n is

$$\delta f_n(\rho) = -\frac{1}{\beta V_n}\ln\left[\frac{\int_0^\rho \mathrm{d}x\exp(-\beta V_n G_{n,s})}{\int_0^\rho \mathrm{d}x\exp(-\beta V_n G_{n,l})}\right] \tag{15}$$

$$2G_{n,i}(\rho,x) = f_{n,i}(\rho+x) + f_{n,i}(\rho-x) - 2f_{n,i}(\rho), \quad i = s,l \tag{16}$$

$$f_{n,l}(\rho) = f_{n-1} + am^2\rho^2 \tag{17}$$

$$f_{n,s}(\rho) = f_{n-1}(\rho) + am^2\rho^2\frac{\Phi\omega^2}{2^{2n+1}L^2} \tag{18}$$

$$a = -\frac{1}{2}\int_\Omega \mathrm{d}\mathbf{r}u^{\mathrm{LJ}}(r) = 8\pi\varepsilon d^3\left(\frac{1}{3}x^{-3} - \frac{1}{9}x^{-9}\right) \tag{19}$$

$$a\omega^2 = \frac{1}{3!}\int_\Omega \mathrm{d}\mathbf{r}r^2u^{\mathrm{LJ}}(r) = \frac{8}{3}\pi\varepsilon d^2\left(x^{-1} - \frac{1}{7}x^{-7}\right) \tag{20}$$

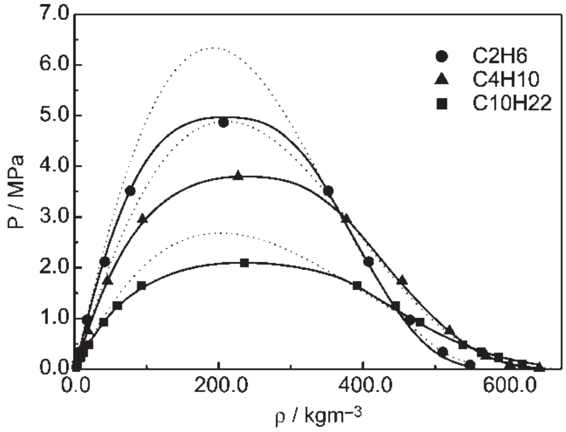

FIGURE 1 Vapor–liquid coexistence lines for *n*-alkanes. Solid lines: this work with RG correction; dotted lines: EOS without RG correction; points: experimental data [14].

L is the cutoff length, and $x = (d + d_{T=T_c})/2d$. Φ is the average gradient of the wavelet and is an adjustable parameter. For mixtures, the following mixing rule is used:

$$\Phi_x = \frac{\sum_{i=1}^{K}\sum_{j=1}^{K} x_i x_j m_i m_j (\Phi_i + \Phi_j)/2}{m^2}. \qquad (21)$$

CALCULATION RESULTS

Vapor–liquid Equilibria

For non-polar and polar fluid, four parameters (m, σ, ε/k and Φ) are necessary to be regressed to account for segment number, segment diameter, segment dispersion energy and the average gradient of the wavelet function. For associating fluids, another dipole moment density-dependent parameter c is added. Some results of vapor–liquid equilibria for *n*-alkanes, ketones and water are shown in Figs. 1–3. For most fluids studied, deviations between calculated values with experimental data [14,15] are about 2% for saturated pressures and saturated liquid densities up to the critical points. For critical temperature, pressure and density, mean deviations are about 1%.

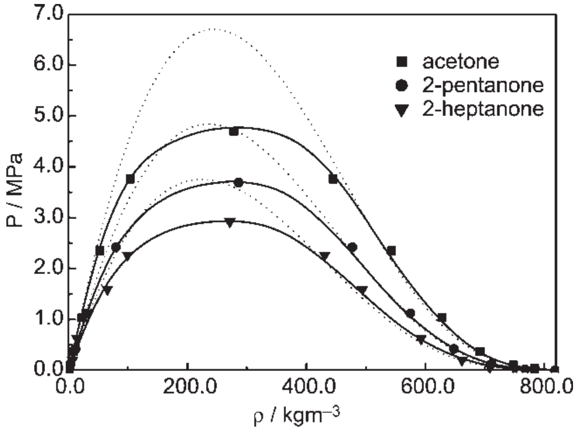

FIGURE 2 Vapor–liquid coexistence curves for ketones. Solid lines: this work with RG correction; dotted lines: EOS without RG correction; points: experimental data [14].

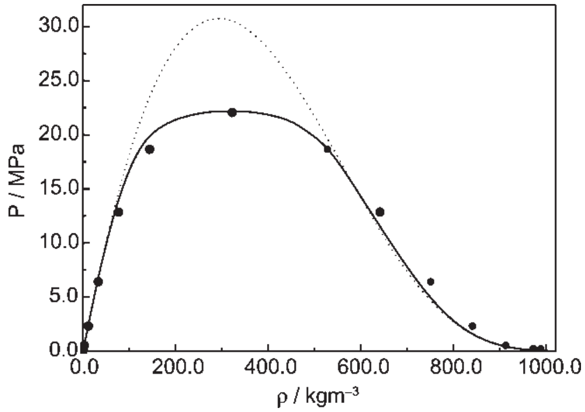

FIGURE 3 Vapor–liquid coexistence lines for water. Solid line: this work with RG correction; dotted line: EOS without RG correction; points: experimental data [15].

Figures 1–3 also show the calculation results of coexistence curve using the simplified SAFT EOS without and with the RG correction. The simplified SAFT EOS without the RG correction gives average deviations of 3.4 and 10.6% for saturated pressures and liquid densities of water, respectively. The EOS with the RG correction gives average deviations of 0.6 and 2.3%.

Phase Equilibria for Binary Mixtures

Because of RG theory's extensive computations, calculation phase equilibria of mixtures described here are much more complex than those using conventional methods with a classical EOS. Parameters k_{ij} and k_{ji} are changed with temperature of binary mixtures. The calculation results for the binary ethane + pentane mixture [16] shown in Fig. 4 reveal the simplified SAFT EOS with the RG correction can

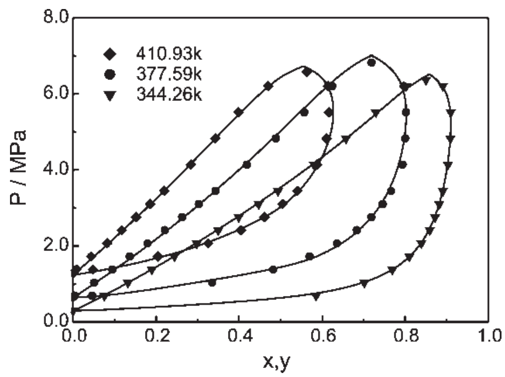

FIGURE 4 Vapor–liquid equilibrium lines for ethane + pentane mixtures. Solid lines: this work with RG correction; points: experimental data [16].

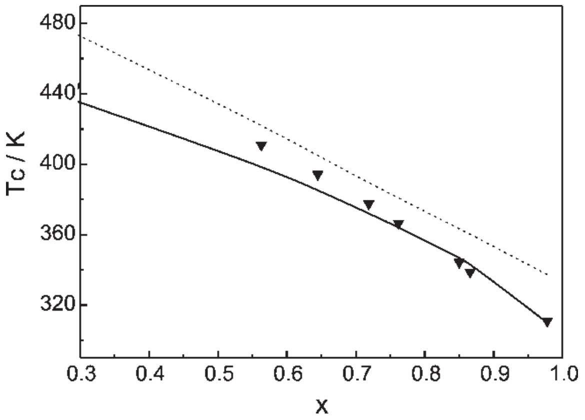

FIGURE 5 Critical temperatures for ethane + pentane mixture. Solid lines: this work with RG correction; dotted lines: this work without RG correction; points: experimental data [16].

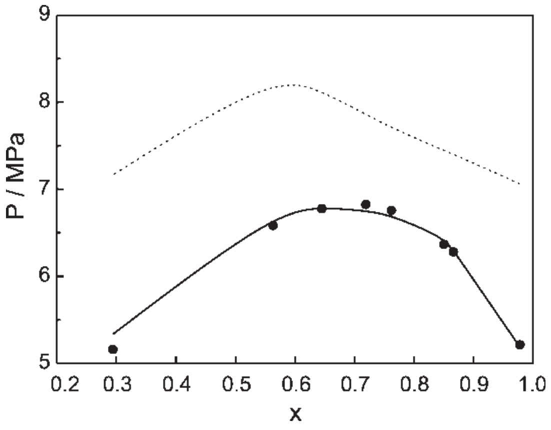

FIGURE 6 Critical pressures for ethane + pentane mixture. Solid lines: this work with RG correction; dotted lines: this work without RG correction; points: experimental data [16].

correctly describe phase equilibria for binary mixtures both far from and near to critical point.

Critical Lines for Binary Mixtures

Figures 5 and 6 show critical temperatures and pressures for binary mixtures of C_2H_6—C_5H_{12} as a function of composition [16]. The EOS without the RG correction overestimates both the critical temperatures and critical pressures while the EOS with the RG correction satisfactorily describes the measured critical lines.

CONCLUSION

Based on SAFT for LJ fluids and RG theory, an equation of state is proposed to describe the properties of non-polar chain fluids, polar chain fluids, associating chain fluids and non-polar chain binary mixtures up to the critical region. The important role of density fluctuation in the critical region is taken into account. The new EOS yields improved description of the vapor–liquid equilibria for pure fluids and binary mixtures, especially in the critical region.

Acknowledgements

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