Phase Equilibria for Chain-Fluid Mixtures Near to and Far from the Critical Region

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A recently established crossover equation of state for pure chain fluids is extended to chain-fluid mixtures. Far from the critical region, where density fluctuations are small, it reduces to the classic equation of state. Near or at the critical point, the crossover equation of state incorporates contributions form long-wavelength density fluctuations. Using segment–segment parameters for pure components and one cross parameter k_{12} for every binary pair as obtained from vapor–liquid equilibrium data remote from the critical region, this crossover equation of state gives vapor–liquid equilibria in good agreement with experiment for binary asymmetric mixtures of n-alkanes far from, near to, and at the critical point.

Introduction

Critical conditions are sometimes encountered in some industrial operations, especially in production and subsequent processing of petroleum and natural gas. Near the critical region, retrograde condensation is often observed. For quantitative process calculations, we require an equation of state (EOS) for mixtures that is valid near to or far from critical conditions. An EOS that meets this requirement is called a crossover EOS. This work presents a crossover EOS for chain-fluid mixtures.

To illustrate retrograde condensation, Figure 1 shows the pressure-temperature loci for a mixture at fixed composition. The solid line is the bubble-point curve and the dashed line is the dew-point curve; they join at critical point C where the two phases become identical. Point C shows the limiting condition where the system can exist in two phases. Near the critical point, the density-dependent properties change dramatically with small changes in temperature or pressure. One century ago, Kuenen (1893, 1897) first observed isothermal retrograde condensation shown in line 1; isobaric retrograde vaporization, shown in line 2, was observed by Duhem (1896, 1901). The maximum pressure at point A is called cricondenbar or maxcondenbar, and the maximum temperature at point B is called cricondentherm or maxcondentherm (Sage et al., 1934). These points give the upper bounds where phase separation can take place. Quantitative understanding of these phase-equilibrium phenomena is useful for design of production, storage, and transportation of fossil-fuel products.

Although extensive experimental studies have been reported (for a review, see Dohrn and Brunner, 1995), it has been difficult to develop a universal model to describe the thermodynamic properties and phase behavior of fluid mixtures at high pressures over a wide range of conditions, including the critical region. Most previous studies are concerned with empirical or phenomenological correlations for vapor–liquid equilibria (VLE) (such as Chao and Seader, 1961; Dastur and Thodos, 1963; Stevens and Thodos, 1963; Van Horn and Kobayashi, 1968; Reid et al., 1987); these studies use any one of several popular EOSs, such as RK (Redlich and Kwong, 1949), SRK (Soave, 1972), and PR (Peng and Robinson, 1976). These cubic EOSs provide improvement over the original van der Waals EOS (van der Waals, 1873) through modifications of the attraction terms as reviewed by Yelash and Kraska (1999). A recent review was given by Wei and Sadus on EOSs for fluid-phase equilibria calculation (2000). It has long been recognized, however, that although these analytical EOSs can describe fluid properties fairly well far away from the critical point, because they are mean-field-based, they fail to reproduce the nonanalytical, singular properties at the critical point, and therefore give poor results in the critical region (Ma, 1976; Domb, 1996). Mean-field theories assume that the immediate environment

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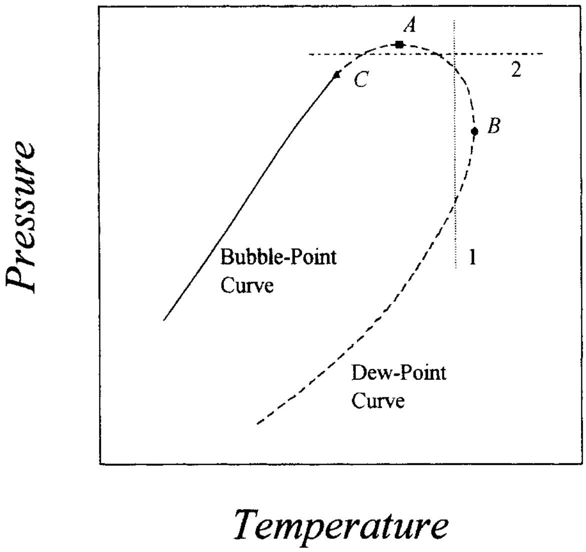

Figure 1. Retrograde-condensation (vaporization) phenomena.

Solid curve: bubble point; dashed curve: dew point. C: critical point; A: cricondenbar; B: cricondentherm. Line 1: isothermal retrograde condensation; line 2: isobaric retrograde vaporization.

of each particle in a fluid has the same composition and density as those of the bluk fluid. Mean-field theories neglect density fluctuations that become large near the critical point (Greer and Moldover, 1981; Sengers and Levelt-Sengers, 1986; Fisher, 1998). Levelt-Sengers (1999) gives a detailed historical review of the weaknesses and strengths of mean-field theories.

Although the inability of mean-field theories to describe critical behavior has been known for many years, a method for corrections became available only relatively recently. Taking long-range density fluctuations into account, scaling and crossover theory can correct mean-field theory. The crossover theory developed by Sengers and coworkers (Edison et al., 1998; Anisimov et al., 1999; Povodyrev et al., 1999), by Anisimov et al. (1995), and by Kiselev and coworkers (Kiselev, 1998; Kiselev and Friend, 1999; Kiselev and Ely, 1999) incorporates a crossover from singular thermodynamic behavior at the critical point to regular thermodynamic behavior far away from the critical point. In this way, a common engineering EOS can be modified for use near the critical point and to yield correct critical behavior. However, the necessary modifications are far from trivial and they need many system-dependent parameters.

The optimized random-phase approximation leads to hierarchical reference theory (HRT) (Parola and Reatto, 1984, 1985; Meroni et al., 1990). HRT can be considered as an exact reformulation of Ornstein-Zernike integral theory, including density fluctuations at all length scales; it can also be taken as a liquid-state implementation of the renormalization-group (RG) theory. Although HRT has been successfully applied to Lennard-Jones fluids and to binary mixtures (Parola and Reatto, 1991; Reatto and Parola, 1996; Pini et al., 1998c), reduction to practice is tedious. A thermodynamically self-consistent Ornstein-Zernike integral theory developed by Stell and coworkers (Pini et al., 1998a,b) provides thermodynamic properties, critical points, and coexistence curves for a lattice gas and for a hard-core Yukawa fluid that compare well with computer simulations. But this integral theory, at present restricted to spherical molecules, has not been reduced to practice.

Recently, White and coworkers (White, 1992; White and Zhang, 1993, 1998) developed a global RG theory based on the Nobel-Prize-winning RG theory of Wilson (1971a,b, 1983). When extended beyond the range of the original RG theory, it can be successfully applied beyond the critical region. The major advantage of White's work is that only a few parameters are required; these have a molecular basis in terms of microscopic intermolecular interactions.

Lue and Prausnitz (1998a,b) extended the accuracy and range of White's RG transformation through an improved Hamiltonian. Good representations of thermodynamic properties and phase equilibria were obtained for pure fluids and their binary mixtures using analytical formulae for square-well (SW) model fluids (Tang and Lu, 1993, 1994, 1995). Tang (1998), and White (1999, 2000) have applied this theory to Lennard-Jones fluids. However, all of these publications are confined to fluids containing simple spherical molecules. Fornasiero et al., (1999) also reported an attempt to apply White's theory to nonspherical molecules using a cubic EOS.

Based on the work of Lue and Prausnitz (1998a,b), Jiang and Prausnitz (1999) developed a crossover EOS for pure chain fluids (EOSCF+RG) by incorporating contributions from long-wavelength density fluctuations using RG theory. Outside the critical region, the crossover EOSCF+RG reduces to a classic EOS for chain molecules (Hu et al., 1996, 1999; Liu and Hu, 1998; Jiang et al., 1998) equivalent to the SAFT equation (Chapman et al., 1990; Huang and Radosz, 1990, 1991); inside the critical region, it gives nonclassic universal critical exponents. This crossover EOS has been used to determine the critical properties of hydrocarbon mixtures (Jiang and Prausnitz, 2000).

This work concerns vapor–liquid equilibria for mixtures of chain fluids. To illustrate applicability, we calculate VLE as well as critical properties and cricondertherms for asymmetric binary mixtures of n-alkane; we compare calculated and experimental results.

Far from the Critical Region

For a mixture of chain fluids, we represent each molecule as a homosegmented chain with number density ρ_i, chain length m_i, and segment diameter σ_i. Interaction between nonbonded chain segments is given by a square-well (SW) potential:

$$u_{ij}(r)=\begin{cases}\infty & r<\sigma_{ij}\\ -\varepsilon_{ij} & \sigma_{ij}<r<\lambda_{ij}\sigma_{ij}\\ 0 & r>\lambda_{ij}\sigma_{ij},\end{cases} \tag{1}$$

where σ_{ij} is an additive hard-sphere diameter given by

$$\sigma_{ij}=\frac{\sigma_i+\sigma_j}{2}. \tag{2}$$

Parameters ε_{ij} and λ_{ij}, denoting depth of the SW interaction potential and the reduced width for pair ij, respectively, are related to corresponding parameters for pure components by

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j}\,(1 - k_{ij}) \tag{3}$$

$$\lambda_{ij} = \frac{\lambda_i \sigma_i + \lambda_j \sigma_j}{\sigma_i + \sigma_j}, \tag{4}$$

where cross parameter k_{ij} is obtained from binary experimental data remote from critical conditions. When $k_{ij} = 0$, Eq. 2 and 3 are the well-known Lorentz (energy)-Berthelot (size) approximation (Rowlinson and Swinton, 1982).

Without loss of generality, but with a view toward fitting experimental data for alkanes, we assume that ε_i depends on temperature T as proposed by Chen and Kreglewski (1977):

$$\varepsilon_i = \varepsilon_i^0 (1 + e/k_B T), \tag{5}$$

where k_B is Boltzmann's constant, and e/k_B is a constant equal to 5 K. Following Barker-Henderson (BH) theory (1967a,b), the temperature dependence of the effective diameter σ_i is

$$\sigma_i = \sigma_i^0 \left[1 - C \exp\left(-3\varepsilon_i^0/k_B T\right)\right], \tag{6}$$

where σ_i^0 is a temperature-independent diameter, and C is an integration constant; following Chen and Kreglewski (1977), we set $C = 0.12$.

The Helmholtz energy density f, that is, the Helmholtz energy per unit volume, has four contributions from ideal-gas, hard-sphere, attractive SW, and chain formation, respectively,

$$f^{\text{EOSCF}} = f^{\text{id}} + f^{\text{hs}} + f^{\text{sw}} + f^{\text{chain}}. \tag{7}$$

The ideal-gas contribution is given by (Lee, 1988)

$$f^{\text{id}} = k_B T \Sigma_i \left[\rho_i \ln(\rho_i \Lambda_i^3) - \rho_i\right], \tag{8}$$

where Λ_i denotes the de Broglie thermal wavelength of molecule i.

The hard-sphere interaction, given by Boublik (1970) and Mansoori et al. (1971), is the so-called BMCSL equation

$$f^{\text{hs}} = k_B T \left[\left(\zeta_2^3/\zeta_3^2 - \zeta_0\right) \ln \Delta + \frac{\pi \zeta_1 \zeta_2/2 - \zeta_2^3/\zeta_3^2}{\Delta} + \frac{\zeta_2^3/\zeta_3^2}{\Delta^2} \right], \tag{9}$$

where $\zeta_l = \Sigma_i m_i \rho_i \sigma_i^l$ and $\Delta = 1 - \pi\zeta_3/6$.

The contribution from the SW attractive potential is estimated by the second-order Baker-Henderson perturbation theory (Barker and Henderson, 1967a, b)

$$f^{\text{sw}} = \frac{1}{\zeta_0} \Sigma_i \Sigma_j m_i m_j \rho_i \rho_j \left(a_1^{ij} + a_2^{ij}/k_B T\right). \tag{10}$$

The mean-attractive energy a_1^{ij} is given by a compact expression from the mean-value theorem (Gil-Villegas et al., 1997; Galindo et al., 1998; McCabe et al., 1998, 1999; McCabe and Jackson, 1999)

$$a_1^{ij} = -2/3 \pi \zeta_0 \sigma_{ij}^3 \varepsilon_{ij} \left(\lambda_{ij}^3 - 1\right) g_{ij}^{\text{hs}}\left(\sigma_{ij}, \zeta_3^{\text{eff}}\right), \tag{11}$$

where the pair correlation function of hard spheres at contact is evaluated at an effective ζ_3^{eff},

$$g_{ij}^{\text{hs}}(\sigma_{ij}) = \frac{1}{\Delta} + \frac{\pi \sigma_i \sigma_j \zeta_2}{4\Delta^2 \sigma_{ij}} + \frac{\pi^2 \sigma_i^2 \sigma_j^2 \zeta_2^2}{72 \Delta^3 \sigma_{ij}^2}, \tag{12}$$

with

$$\zeta_3^{\text{eff}} = c_1 \zeta_3 + c_2 \zeta_3^2 + c_3 \zeta_3^3. \tag{13}$$

Coefficients c_n are calculated by the matrix (Gil-Villegas et al., 1997; Galindo et al., 1998; McCabe et al., 1998, 1999; McCabe and Jackson, 1999):

$$\begin{pmatrix} c_1 \\ c_2 \\ c_3 \end{pmatrix} = \begin{pmatrix} 2.25855 & -1.50349 & 0.249434 \\ -0.669270 & 1.40049 & -0.827739 \\ 10.1576 & -15.0427 & 5.30827 \end{pmatrix} \begin{pmatrix} 1 \\ \lambda_{ij} \\ \lambda_{ij}^2 \end{pmatrix}, \tag{14}$$

The second perturbation term a_2^{ij} describing fluctuations of the attractive energy is given by

$$a_2^{ij} = \frac{\varepsilon_{ij} \zeta_0^2 \Delta^4}{2\left(\zeta_0 \Delta^2 + \pi \zeta_1 \zeta_2 \Delta + \pi^2 \zeta_2^3/4\right)} \frac{\partial a_1}{\partial \zeta_0}. \tag{15}$$

The contribution from chain formation is (Hu et al., 1996; Chapman et al., 1990)

$$f^{\text{chain}} = k_B T \Sigma_i \rho_i (1 - m_i) \ln y_{ii}^{\text{sw}}(\sigma_i), \tag{16}$$

where cavity correlation function $y_{ij}^{\text{sw}}(\sigma_{ij})$ at contact is defined by

$$y_{ij}^{\text{sw}}(\sigma_{ij}) = g_{ij}^{\text{sw}}(\sigma_{ij}) \exp(-\varepsilon_{ij}/k_B T), \tag{17}$$

with

$$g_{ij}^{\text{sw}}(\sigma_{ij}) = g_{ij}^{\text{hs}}(\sigma_{ij}) + \frac{1}{2\pi k_B T \sigma_{ij}^3} \left(3 \frac{\partial a_1^{ij}}{\partial \zeta_0} - \frac{\lambda_{ij}}{\zeta_0} \frac{\partial a_1^{ij}}{\partial \lambda_{ij}}\right). \tag{18}$$

Near the Critical Region

The preceding equations constitute the EOS for chain fluids (EOSCF) without RG corrections for a mixture. EOSCF performs well only far from the critical region where density fluctuations are very small. Approaching the critical point, however, the correlation length increases, and long-wavelength density fluctuations become important, diverging to infinity at the critical point. Large correlation lengths imply that the system is not homogeneous near the critical point; correlations between larger and larger numbers of molecules make an increasingly significant contribution to the Helmholtz energy.

As shown by several early studies (Fisher, 1968; Griffiths and Wheeler, 1970; Leung and Griffiths, 1973; Saam, 1970), the behavior of a mixture near the critical point can be related to that of a pure fluid. It was based on the principle of critical-point universality, that is, the nonclassic critical exponents and scaling laws of a mixture have the same values and form as those of a pure fluid. In establishing this relation, the "generalized coordinates" (those that have different values in coexisting phases, like density, composition) should be transformed into "generalized forces" (that is, field variables that are equal in coexisting phases, like temperature, pressure, chemical potential). The thermodynamic relations for a mixture should be described in terms of independent field variables. The model proposed by Leung and Griffiths (1973) was modified by Moldover and Rainwater (1988) and has been applied to study vapor–liquid equilibria of a large number of binary mixtures, including electrolyte solutions (Belyakov et al., 1997; Kiselev and Rainwater, 1998). In the same spirit, Fox (1979, 1983) developed a mathematical method to incorporate the correct nonclassic critical behavior into the classic equation of state. This method has been extended by de Pablo and Prausnitz (1989, 1990) to study liquid–liquid equilibria of binary and ternary systems.

On the other hand, Anisimov et al. (1971) found that all thermodynamic properties of a binary mixture along the critical isochore can be determined by two cones, a wide cone and a narrow one. For all real fluid mixtures, the characteristic temperature of the narrow cone is extremely small; under this condition, the thermodynamic relations can be reasonably simplified in terms of density variables and can be used to describe thermodynamic properties except very close to the critical point. Very recently, this principle has been applied by Kiselev and Friend (1999) with cubic crossover EOS (Kiselev, 1998) described by density variables for mixtures.

Based on this principle, we write our crossover EOS for mixtures in terms of density variables. Following the work of White (White, 1992; White and Zhang, 1993, 1998), Lue and Prausnitz (1998a,b), and Jiang and Prausnitz (1999), incorporation of contributions from density fluctuations with increasingly longer wavelengths leads to EOSCF + RG. Recursion relations are used to evaluate the Helmholtz energy density:

$$f_n(\rho) = f_{n-1}(\rho) + \delta f_n(\rho) \tag{19}$$

$$\delta f_n(\rho) = -K_n \ln \frac{\Omega_n^s(\rho)}{\Omega_n^l(\rho)}, \qquad 0 \le \rho < \rho^{\max}/2 \tag{20a}$$

$$\delta f_n(\rho) = 0, \qquad \rho^{\max}/2 \le \rho < \rho^{\max}. \tag{20b}$$

The zero-order solution f_0 is approximated by Eq. 7; Ω_n^l and Ω_n^s are integrals over the amplitudes of the density fluctuations for long-range attraction and for short-range attraction, respectively; ρ is total number density, $\rho^{\max}$ is the maximum possible density, and

$$K_n = \frac{k_B T}{2^{3n} L^3} \tag{21}$$

$$\Omega_n^a(\rho) = \int_0^{\rho_1} \dots \int_0^{\rho_M} \exp\left[-\bar{E}_n^a(\rho, z)/K_n\right] dz_1 \dots dz_M, \qquad \alpha = s, l \tag{22}$$

$$\bar{E}_n^a(\rho, z) = \frac{\bar{f}_n^a(\rho + z) + \bar{f}_n^a(\rho - z)}{2} - \bar{f}_n^a(\rho), \qquad a = s, l \tag{23}$$

$$\bar{f}_n^l(\rho) = f_{n-1}(\rho) + \Sigma_i \Sigma_j b_{ij} \rho_i \rho_j \tag{24}$$

$$\bar{f}_n^s(\rho) = f_{n-1}(\rho) + \Sigma_i \Sigma_j b_{ij} \rho_i \rho_j \frac{\Phi_{ij} \xi_{ij}^2}{2^{2n+1} L_{ij}^2}, \tag{25}$$

where z_i ($i = 1, 2, \dots, M$; M is the total number of components) is the integral variable within $[0, \rho_i]$; b_{ij} is the interaction volume and ξ_{ij} refers to the range of the attractive potential. They are related to the parameters of the SW potential by

$$b_{ij} = \frac{2\pi}{3} \varepsilon_{ij} (\lambda_{ij} \sigma_{ij})^3 \tag{26}$$

$$\xi_{ij} = \frac{1}{\sqrt{5}} (\lambda_{ij} \sigma_{ij}). \tag{27}$$

Parameter L_{ij} is the cutoff length; we use the same L for all components. Φ_{ij} is the average gradient of the wavelet function (Battle, 1992, 1994), given by

$$\Phi_{ij} = \frac{\Phi_i \sigma_i + \Phi_j \sigma_j}{\sigma_i + \sigma_j}. \tag{28}$$

The preceeding recursion procedure can be interpreted in terms of contributions to the Helmholtz energy density; this procedure gives the ratio of non-mean-field contributions to mean-field contributions at gradually increasing long wavelengths. In principle, the recursion should be performed until index n approaches infinity; however, we find that $n = 5$ is sufficient. For binary mixtures considered here, we perform the calculations numerically with the density step $6/(\pi m_i \sigma_i^3 500)$ for each component; we then smooth the stepwise Helmholtz energy density with a two-dimensional cubic spline function (Press et al., 1992).

Table 1. Cross-Parameter k_{ij} for Binary Mixtures of CH_4 Series and C_2H_6 Series Evaluated from Experimental Data Remote from Critical Conditions

Comp. j	$k_{ij}(i = CH_4)$	Data Source	$k_{ij}(i = C_2H_6)$	Data Source
C_2H_6	0.0048	Knapp et al. (1982)		
C_3H_8	0.0150	Knapp et al. (1982)	0.0095	Knapp et al. (1982)
n-C_4H_{10}	0.0255	Knapp et al. (1982)	0.0163	Knapp et al. (1982)
n-C_5H_{12}	0.0381	Knapp et al. (1982)	0.0220	Knapp et al. (1982)
n-C_6H_{14}	0.0490	Knapp et al. (1982)	0.0263	Knapp et al. (1982)
n-C_7H_{16}	0.0584	Knapp et al. (1982)	0.0312	Knapp et al. (1982)
n-C_8H_{18}	0.0704	Knapp et al. (1982)	0.0375	Knapp et al. (1982)
n-C_9H_{20}	0.0801	Knapp et al. (1982)		
n-$C_{10}H_{22}$	0.0874	Knapp et al. (1982)	0.0455	Knapp et al. (1982)
n-$C_{12}H_{26}$	0.0910	Rijkers et al. (1992)	0.0485	Lee et al. (1969)
n-$C_{16}H_{34}$	0.0920	Glaser et al. (1985)	0.0495	Goede et al. (1989)
n-$C_{20}H_{42}$	0.0932	Darwish et al. (1993) Huang et al. (1988b)	0.0489	Peters et al. (1987) Peters et al. (1988)
n-$C_{28}H_{58}$	0.0930	Darwish et al. (1993) Huang et al. (1988a)	0.0487	Gasem et al. (1989) Huang et al. (1988a)
n-$C_{36}H_{74}$	0.0937	Darwish et al. (1993) Huang et al. (1987)	0.0490	Gasem et al. (1989) Huang et al. (1987)

After we calculate the Helmholtz energy density of the system, pressure and chemical potential are obtained from

$$P = -f + \rho\left(\frac{\partial f}{\partial \rho}\right)_T \tag{29}$$

$$\mu_i = \left(\frac{\partial f}{\partial \rho_i}\right)_{T,V,\rho_{j[i]}}, \tag{30}$$

where N is the total number of molecules and V is the total volume.

Results and Discussion

Segment–segment parameters for pure n-alkanes from methane to n-hexatriacontane have been correlated previously (Jiang and Prausnitz, 1999). The chain length is estimated from a simple empirical relation with carbon number C_i by $m_i = 1 + (C_i - 1)/3$. Interaction potential ε_i^0, segment diameter σ_i^0, and square-well width λ_i are optimized to fit experimental vapor pressures and saturated liquid densities at temperatures 20% below critical temperature T_c and experimental isotherms pVT at temperatures 20% above T_c (Smith and Srivastava, 1986; Vargaftik, 1983). To incorporate contributions from long-wavelength density fluctuations inside the critical region, we set cutoff length $L = 11.5$ Å and select a suitable parameter Φ_i to fit the experimental pure-component critical properties.

For pure chain fluids, we compare our work with similar work of Kiselev and Ely (1999). For vapor–liquid equilibrium behavior, both give satisfactory results; however, for pVT properties, Kiselev and Ely's work is slightly better than ours, because there are more adjustable parameters in their work. For pure components, in addition to the parameters in the classic EOS, in their work there are three adjustable parameters (Gi, d_1, and v_1; another parameter δ_1 is set constant); however, in our work there is only one adjustable parameter (Φ; another parameter L is set constant).

We fit cross-parameter k_{ij} to experimental vapor–liquid equilibrium data remote from the critical region for binary n-alkanes mixtures containing CH_4 or C_2H_6. Near to the critical region, cross-parameter Φ_{ij} given by Eq. 28 for a binary mixture is input to calculate phase behavior. Table 1 gives the optimized k_{ij} and corresponding data sources. Figure 2 shows that parameter k_{ij} rises linearly with low carbon number of the second component, and then rapidly approaches a constant. Triangles are for binary mixtures containing CH_4; circles are for those containing C_2H_6. The trend shown in Figure 2 was observed more than 20 years ago (Donohue and Prausnitz, 1978). Upon increasing the carbon number of the second component, the rising difference between the two components raises k_{ij}. However, upon further increase in carbon number (chain length) of the second com-

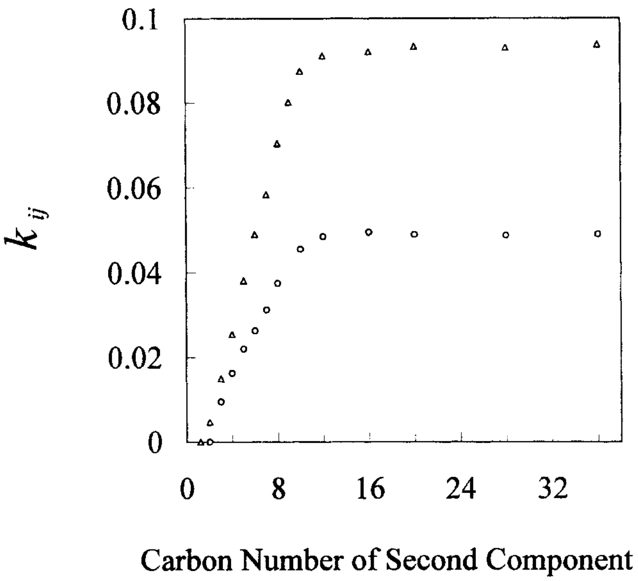

Figure 2. Dependence of cross-parameter k_{ij} on the carbon number of the second component.
Triangles, CH_4 series; circles, C_2H_6 series.

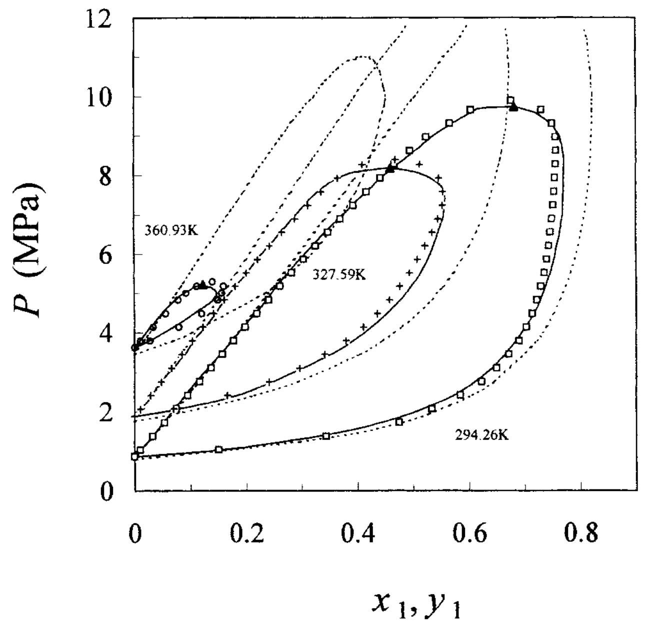

Figure 3a. Vapor liquid equilibria for $CH_4(1)$-$C_3H_8(2)$ mixtures.

Open points, experiment; dashed lines, EOSCF; solid lines, EOSCF+ RG; solid triangles, critical points.

ponent, the first component cannot "see" the increasing difference between itself and the second components; therefore, k_{ij} becomes constant.

Figure 3a shows vapor–liquid equilibria for binary mixtures of CH_4 with C_3H_8; Figure 3b shows the corresponding equilibrium ratios defined by

$$K_i = y_i/x_i, \tag{31}$$

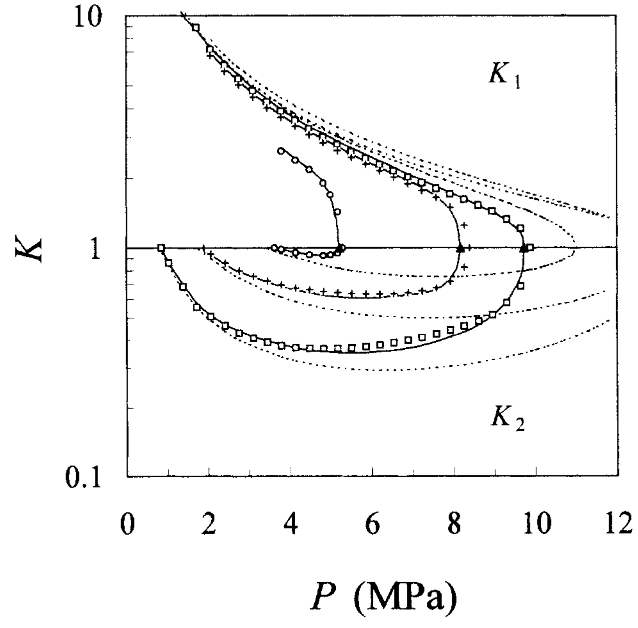

Figure 3b. Equilibrium ratios for $CH_4(1)$-$C_3H_8(2)$ mixtures (legend as in Figure 3a).

where y and x refer to mol fraction in the vapor phase and liquid phase, respectively. The open points represent experimental data (Knapp et al., 1982); dashed and solid lines are calculated from EOSCF and EOSCF + RG, respectively. The critical points, indicated by solid triangles, are estimated by extrapolation of a K-P plot to $K = 1.0$, as recommended by Sage and others (Sage et al., 1940, 1942; Reamer et al., 1950; Kahre, 1974). At the critical point, we have

$$\left(\frac{\partial P}{\partial x_1}\right)_T = \left(\frac{\partial P}{\partial y_1}\right)_T = 0 \quad \text{at} \quad x_1 = y_1 \tag{32}$$

and

$$\left(\frac{\partial P}{\partial K_1}\right)_T = \left(\frac{\partial P}{\partial K_2}\right)_T = 0 \quad \text{at} \quad K_1 = K_2 = 1. \tag{33}$$

EOSCF is deficient in its description of phase behavior in the critical region; however, EOSCF + RG repairs this deficiency because density fluctuations are reasonably incorporated. Far from the critical region, EOSCF + RG theory reduces to the original EOSCF where the latter is reliable. In general, EOSCF + RG gives good agreement with experiment in both regions.

Figure 4a and 4b show vapor–liquid equilibria and equilibrium ratios for binary mixtures of CH_4 with n-C_4H_{10}. Legends are the same as those in Figure 3a. The solid circle denotes the cricondentherm where

$$\left(\frac{\partial P}{\partial y_1}\right)_T = \infty. \tag{34}$$

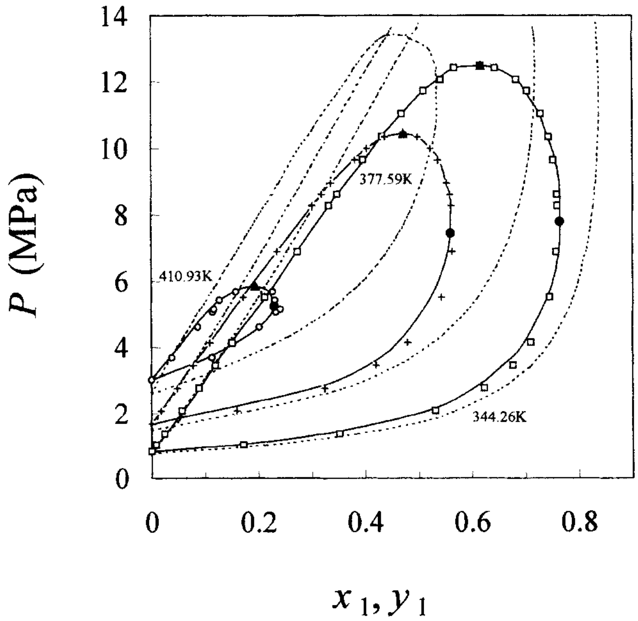

Figure 4a. Vapor–liquid equilibria for $CH_4(1)$-n-$C_4H_{10}(2)$ mixtures.

Open points, experiment; dashes lines, EOSCF; solid lines, EOSCF + RG; solid triangles, critical points; solid circles, cricondentherms.

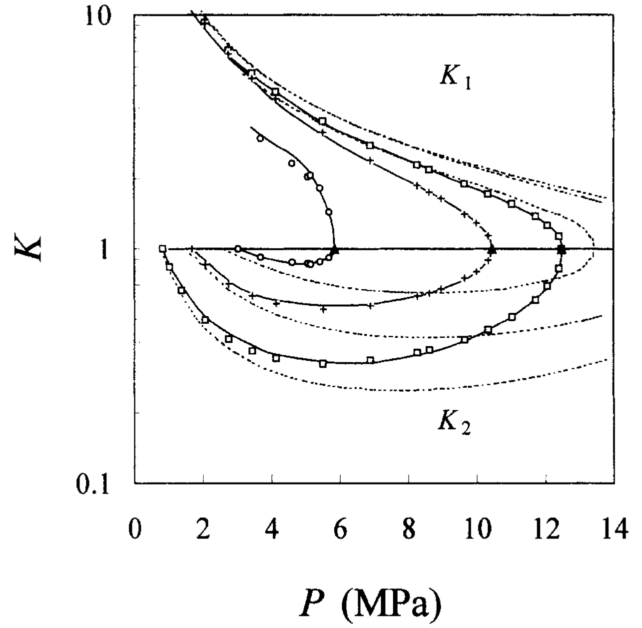

Figure 4b. Equilirium ratios for CH_4(1)–n-C_4H_{10}(2) mixtures (legend as in Figure 3a).

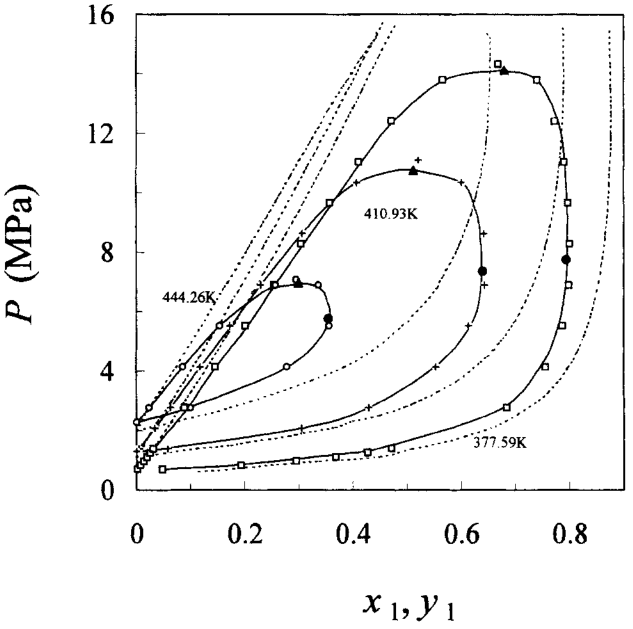

Figure 5a. Vapor–liquid equilibria for CH_4(1)–n-C_5H_{12}(2) mixtures (legend as in Figure 4a).

In a pressure-temperature plot at fixed composition, the cricondentherm condition is

$$\left(\frac{\partial P}{\partial T}\right)_y = \infty. \tag{35}$$

Figure 4c shows critical and cricondentherm properties for binary mixtures of CH_4 with n-C_4H_{10}. Points represent experimental data (Sage et al., 1940), and lines are calculated from EOSCF + RG. Triangles and solid lines denote critical properties; circles and dashed lines show cricondentherm properties. Agreement with experiment is good.

Figure 5, similar to Figure 4, gives results for binary mixtures of CH_4 with n-C_5H_{12}. The experimental data for vapor–liquid equilibria are from Knapp et al. (1982); critical and cricondentherm properties are from Sage (1942), and Berry and Sage (1970).

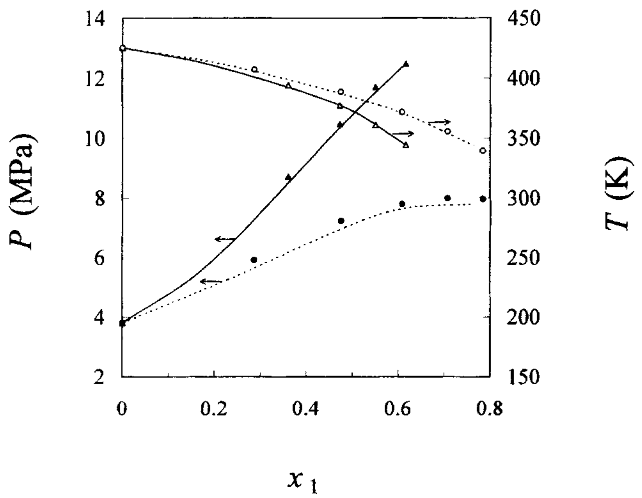

Figure 4c. Critical properties and cricondentherm properties for CH_4(1)–n-C_4H_{10}(2) mixtures.

Triangles and solid lines, critical properties; circles and dashed lines, cricondentherm properties.

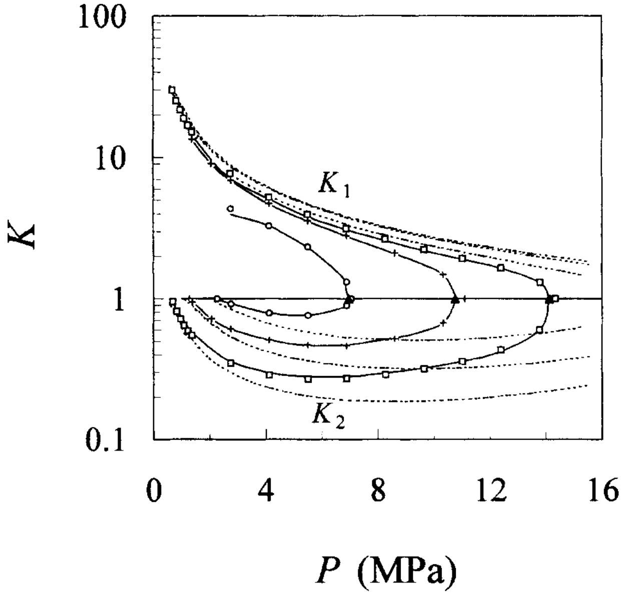

Figure 5b. Equilibrium ratio for CH_4(1)–n-C_5H_{12}(2) mixtures.

Legend as in Figure 4b.

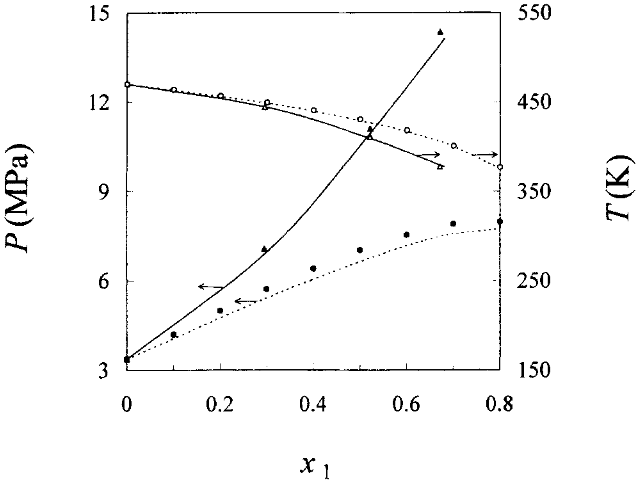

Figure 5c. Critical properties and cricondentherm properties for CH_4(1)–n-C_5H_{12}(2) mixtures.
Legend as in Figure 4c.

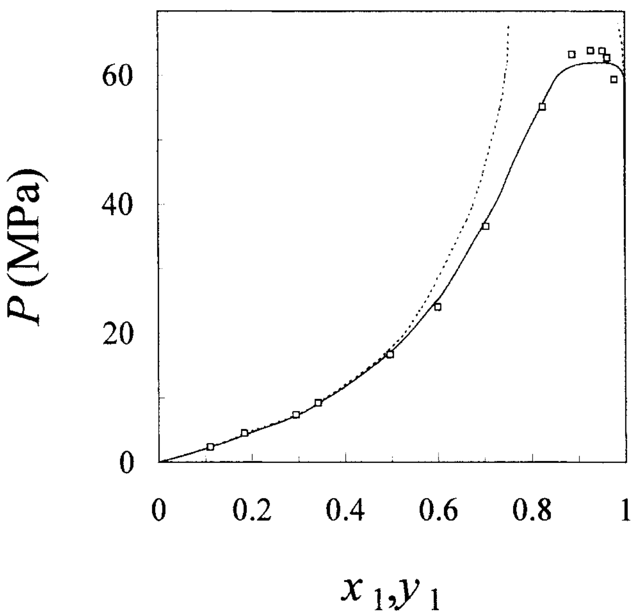

Figure 7. Vapor liquid equilibria for CH_4(1)–n-$C_{16}H_{34}$(2) mixtures at 320.0 K.
Legend as in Figure 3a.

Figures 6 and 7 show vapor–liquid equilibria for binary mixtures of CH_4 with n-$C_{12}H_{26}$ and n-$C_{16}H_{34}$, respectively. The points show experimental data (Rijkers et al., 1992; Glaser et al., 1985); dashed and solid lines are calculated from EOSCF and EOSCF + RG, respectively. EOSCF + RG provides much improvement because it takes into account the contribution from density fluctuations in the critical region.

Figure 8 shows the bubble-point curve for three binary mixtures of CH_4 with n-$C_{20}H_{42}$, n-$C_{28}H_{58}$, and n-$C_{36}H_{74}$. Points show experimental data (Darwish et al., 1993; Huang et al., 1987, 1988a, b); solid lines are calculated from EOSCF + RG. Good agreement is obtained.

Finally, Figure 9 shows vapor–liquid equilibria for binary mixtures of C_2H_6 with n-$C_{20}H_{42}$. Experimental data are from Peters et al. (1987, 1988). Similar to binary mixtures containing CH_4, remote from the critical region, both EOSCF and EOSCF + RG give almost the same results; however, in the critical region, EOSCF + RG is significantly superior.

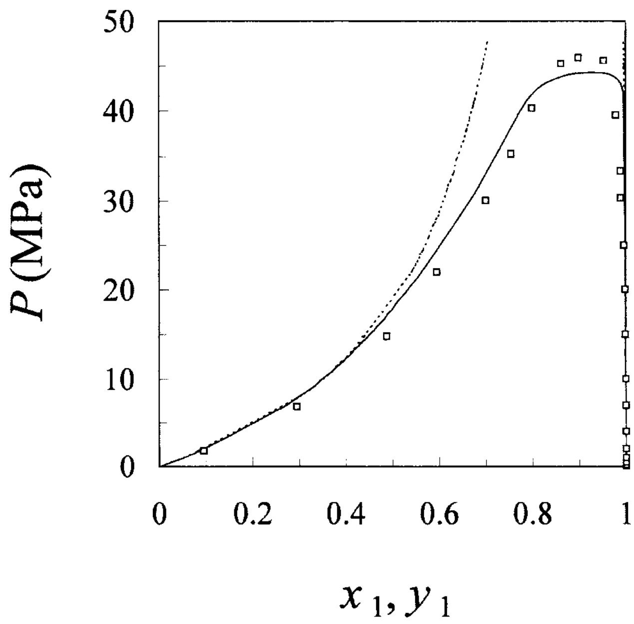

Figure 6. Vapor–liquid equilibria for CH_4(1)–n-$C_{12}H_{26}$(2) mixtures at 303.15 K.
Legend as in Figure 3a.

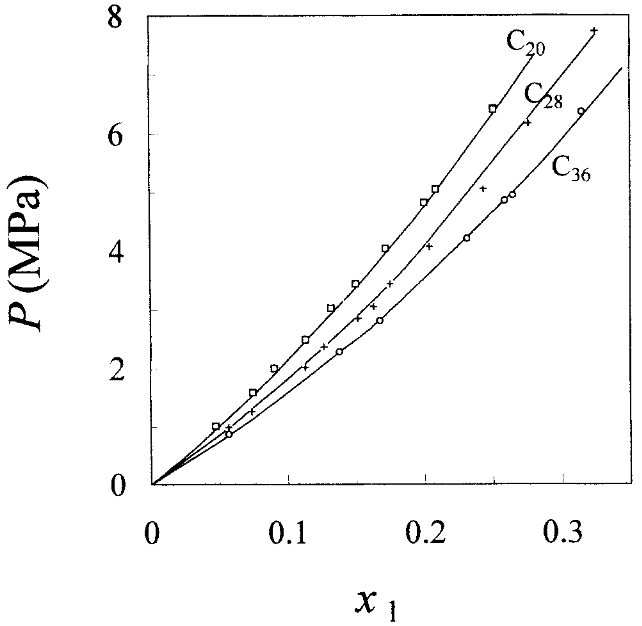

Figure 8. Bubble pressures at 373.15 K for CH_4(1)–n-$C_{20}H_{42}$(2), CH_4(1)–n-$C_{28}H_{58}$(2), and CH_4(1)–n-$C_{36}H_{74}$(2), respectively.
Points, experimental data; lines, EOSCF + RG.

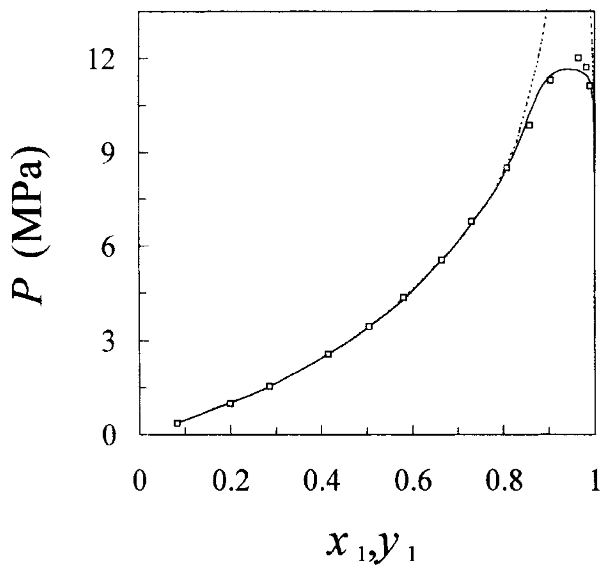

Figure 9. Vapor–liquid equilibria for C_2H_6(1)–n-$C_{20}H_{42}$(2) mixtures at 350.0 K.

Legend as in Figure 3a.

Conclusion

A recently developed crossover equation of state for pure chain fluids, EOSCF + RG, has been extended to mixtures of chain fluids. This EOSCF + RG is able to describe the phase equilibria of mixtures both far from and near to the critical region. Far from the critical region, where density fluctuations are small and RG corrections are negligible, EOSCF + RG reduces to the classic EOSCF. However, near to and in the critical region, where density fluctuations are large, EOSCF fails due to its mean-field nature. Incorporating the essential contribution from density fluctuations, EOSCF + RG significantly improves agreement with experiment.

For the binary mixtures of the n-alkanes illustrated here, we use the square-well segment–segment parameters for pure components from our previous work; in addition, we use cross-parameter k_{ij} optimized by fitting equilibria data remote from the critical region. We find that all parameters vary smoothly with the carbon numbers of the components. Therefore, for those binary n-alkanes systems where experimental data are not available, we can with confidence predict phase equilibria for a wide range of conditions, including the critical region. We can also model n-alkanes as Lennard-Jones chains and optimize the Lennard-Jones segment–segment parameters (Blas and Vega, 1997, 1998a,b).

In general, EOSCF + RG gives good results, much better than those from EOSCF in the critical region. However, we also observe some deviations for EOSCF + RG from experiment. These deviations are not primarily due to RG theory; rather, they result from inadequacies in the classic equation of state remote from critical conditions. Because the classic EOSCF is a first-order perturbation theory, higher-order correlations between the segments in the chain are neglected; also, a crude approximation is used here to subtract contributions from long-wavelength density fluctuations in EOSCF; perhaps, some deviation is due to neglect of many-body interactions (Elrod and Saykally, 1994; Adidharma, and Radosz, 1998; Sadus, 1998a,b; Marcelli and Sadus, 1999) that may be important at high densities.

To use the crossover equation of state described here, the first task is to evaluate numerically the Helmholtz energy density through the recursion relations. We perform these calculations with a suitable density step ρ_i^{max}/N_{step} for each component. In our studies for pure components and binary mixtures, we use $N_{step} = 500$ to achieve good accuracy with reasonable computational time. However, for ternary mixtures, with $N_{step} = 500$, there is not enough memory in our PC to perform the calculations. To maintain accuracy, we cannot significantly reduce N_{step}. The severity of this computational problem grows worse as the number of components in the mixture rises. We are currently making efforts toward solving this computational problem.

While this work discusses the VLE for mixtures of n-alkanes, it can also be used to describe VLE for fluid mixtures containing a polymer like polyethylene (Folie and Radosz, 1995; Luettmer-Strathmann et al., 1998; Orbey, et al., 1998), for liquid–liquid equilibria of mixtures of small molecules (Greer, 1978; Hölscher, et al., 1986) or polymer with solvent (Hino and Prausnitz, 1997; Liu and Hu, 1998; Vetere, 1998), and for solid–fluid equilibria in natural-gas systems (Won, 1986; Suleiman and Eckert, 1995a,b; Flöter, et al., 1997, 1998; Sun and Teja, 1998; Teja et al., 1998; Coutinho, 1998), or for the solubility of a solid polymer in supercritical/compressed fluids (O'Neill, et al., 1998; Pan and Radosz, 1998, 1999).

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Notation

b_{ij} = interaction volume for ij pair
A = Helmholtz energy
C = integration constant in Barker-Henderson theory
f = Helmholtz energy density
$g_{ij}(r)$ = pair correlation function for ij pair
k_B = Boltzmann constant
k_{ij} = cross-parameter for binary mixture ij pair
K_i = equilibrium ratio
L = cutoff length
m_i = chain length of molecule i
M = total number of components
n_i = mol number of component i
N = total number of molecules
N_{step} = step of density
P = pressure
P^c = critical pressure of mixture
r = center-to-center distance
SW = square-well potential
T^c = critical temperature of mixture
u = interaction potential
V = total volume of the system
x_i = mol fraction of component i in the liquid phase

y_i = mol fraction of component i in the vapor phase
$y_{ij}(r)$ = cavity correlation function for ij pair
z = integral variable for density
ρ_i = number density of molecule i
σ_i = segment diameter of molecule (or segment) i
ε_i = SW interaction well depth of molecule (or segment) i
λ_i = SW interaction range of molecule (or segment) i
Λ_i = de Broglie thermal wavelength of molecule i
μ_i = chemical potential of component i
Φ_i = average gradient of wavelet function for component i

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