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A crossover random lattice fluid model for hydrocarbons and carbon dioxide

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Abstract−A random lattice fluid model with finite coordination number is a versatile molecular-based lattice fluid equation of state, but this model fails to reproduce the non-analytical, singular behavior of fluids in the critical region. In this work, a method of obtaining the classical critical properties is presented in the random lattice fluid model. This model is combined with the crossover theory to obtain the crossover random lattice fluid model and to calculate the thermodynamic properties of hydrocarbons and carbon dioxide. This crossover random lattice fluid model presents much better agreement with experimental data near to and far from the critical region than the classical random lattice fluid model.

Key words: Crossover, Random, Lattice Model, Hydrocarbons, Carbon Dioxide

INTRODUCTION

The classical lattice models such as Sanchez-Lacombe lattice equation of state [1,2] have been successfully applied to describe the phase equilibrium of a wide range of industrially important fluids, such as hydrocarbons, polymers and associating fluids. However, the statistical mechanical theories point out that fluids have density fluctuations. Far away from the critical point, the fluctuations affect the thermodynamic properties of fluids slightly and can be neglected. Therefore, mean-field theories [3] can be used to represent the thermodynamic properties of fluids. The mean-field theories assume that the immediate environment of each particle in a fluid has the same composition and density as those of the bulk fluid. Mean-field theories neglect density fluctuations. Near the critical point, the fluctuations of fluids become very large and some singular phenomena and properties, such as the critical emulsification phenomenon, take place. To improve the description of the gas-liquid critical locus for pure fluids, the lattice model parameters can be rescaled [4] to the experimental pure fluid critical point, and an accurate representation of the critical locus is obtained. However, despite the success achieved using a rescaled lattice model, poor agreement is obtained at lower pressures, especially at lower temperatures and for the coexisting liquid densities.

Critical phenomena in fluids have been the subject of many theoretical and experimental studies during the past thirty years. The most striking result of these studies has been the discovery of critical-point universality: The microscopic structure of fluids becomes unimportant in the vicinity of a critical point [5]. The discovery makes it possible to develop universal equations of state for fluids in the critical region and enable us to look into the problem of formulating global equations of state for dense fluids from an entirely new point of view. Because of density fluctuations, some thermodynamic properties, such as the isothermal compressibility and the isochoric heat capacity, change discontinuously in the region around the critical point. Some of them even diverge or become infinite. From experimental data, the limiting values of the differential molar volume, the differential molar enthalpy and the differential molar heat capacity near the critical point are related to the distance from the critical point. In terms of the distance from the critical point, the scaling laws with universal scaling functions and universal critical exponents can characterize the thermodynamic behaviors near the critical point [6].

Many efforts have been made to construct thermodynamic models to accomplish the crossover of near and far from the critical region. Kiselev et al. [7,8] presented a crossover theory which considered density fluctuations and provided successful representations of the thermodynamic properties of fluids over a wide range including the ideal gas limit and the critical region. In a former study [9], the present authors presented the crossover Sanchez-Lacombe lattice fluid model which incorporates the crossover scale laws valid asymptotically close to the critical point while reducing to the original Sanchez-Lacombe lattice fluid model far from the critical point. By the way, the Sanchez-Lacombe model has some weak points such as infinite coordination number limit known as the Flory and inconsistent problem for phase equilibrium calculation [10].

In this study, the random lattice fluid model with finite coordination number is used and a method of obtaining the classical critical properties is presented. This model was combined with the crossover theory [7,8] to obtain the crossover random lattice fluid model and to calculate the thermodynamic properties of supercritical carbon dioxide and hydrocarbons (from methane to n-hexane).

CLASSICAL RANDOM LATTICE FLUID MODEL

Sanchez and Lacombe [1,2] proposed the lattice fluid model to describe thermodynamic properties using the full Guggenheim [11]'s combinatory but took up the large coordination number limit known as the Flory approximation. In this study, the random lattice fluid model with finite coordination number was chosen as a reference lattice fluid model. Following the approach of Panayoutou et al. [12] and Kumar et al. [13] and assuming the random mixing of holes

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and molecules, the random lattice fluid (RLF) equation of state (EOS) was represented as follows:

$$\frac{\tilde{P}}{\tilde{T}} = -\ln(1-\tilde{\rho}) + \frac{z}{2}\ln\left[1+\left(\frac{q}{r}-1\right)\tilde{\rho}\right] - \frac{\theta^2}{\tilde{T}} \tag{1}$$

Here, all the quantities with the tilde (~) denote the reduced variables defined by

$$\tilde{P} = \frac{P}{P^*},\ \tilde{T} = \frac{T}{T^*},\ \tilde{\rho} = \frac{\rho}{\rho^*},\ \rho^* = \frac{1}{rv^*} \tag{2}$$

Where the reducing parameters are defined by

$$P^* v^* = RT^* = \frac{z}{2}\varepsilon^* \tag{3}$$

Here θ is the effective surface area fraction of molecules in the lattice,

$$\theta = \frac{N_1 q_1}{N_q} = \frac{(q/r)\tilde{\rho}}{1+(q/r-1)\tilde{\rho}} \tag{4}$$

Let us set coordination number, z=10 as used in lattice fluid theories of the same genre [12,13].

The RLF EOS has three molecular parameters; ε^*, v^*, and r, which are equivalently of the scale factors T^*, P^*, or ρ^*.

The residual Helmholtz free energy $A^r(T, v)$ was obtained as follows:

$$A^r(T,v) = -\int_{\infty}^{V}\left(P - \frac{nRT}{V}\right)dV = nrRT\left[\left(\frac{1}{\tilde{\rho}}-1\right)\ln(1-\tilde{\rho})\right] - RT\left[\frac{znr}{2\tilde{\rho}} + n(1-r)\right]\ln\left(1+\left(\frac{q}{r}-1\right)\tilde{\rho}\right) + nRT - \frac{nqRT\theta}{\tilde{T}} \tag{5}$$

The molar Helmholtz free energy can be written as:

$$a(T, v) = a^r(T, v) + a^{id}(T, v) \tag{6}$$

where $a^r(T, v)$ is the residual molar Helmholtz free energy and $a^{id}(T, v)$ is the molar Helmholtz free energy for ideal gas

$$a^{id}(T, v) = -RT\ln v + a_0(T) \tag{7}$$

In Eq. (7), $a_0(T)$ is the temperature-dependent part of the Helmholtz free energy for ideal gas.

The classical expression for the Helmholtz free energy $\overline{A}(T, v)$ was rewritten in the dimensionless form as follows:

$$\overline{A}(T,v) = \frac{a(T,v)}{RT} = \overline{A}^r(T,v) - \ln v + \overline{A}_0(T) \tag{8}$$

$$\overline{A}^r(T,v) = r\left[\left(\frac{1}{\tilde{\rho}}-1\right)\ln(1-\tilde{\rho})\right] - \left[\frac{zr}{2\tilde{\rho}} + (1-r)\right]\ln\left(1+\left(\frac{q}{r}-1\right)\tilde{\rho}\right) + 1 - \frac{q\theta}{\tilde{T}} \tag{9}$$

EXPRESSION FOR CRITICAL PROPERTIES

The classical critical parameters T_{oc}, P_{oc} and v_{oc} can be obtained from the condition

$$\left(\frac{\partial P}{\partial \rho}\right)_{T_{oc}} = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_{oc}} = 0 \tag{10}$$

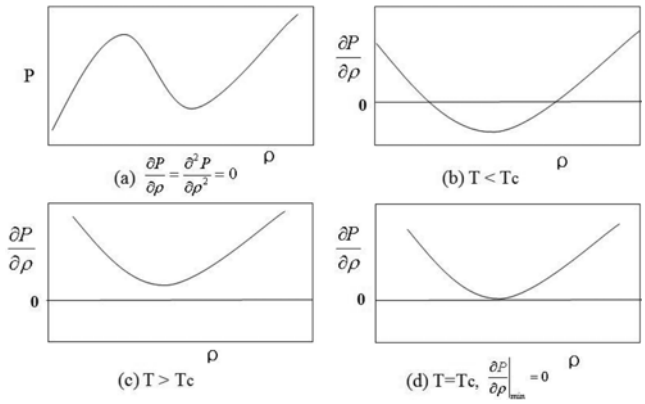

Fig. 1. A method of classical critical properties for the random lattice fluid (RLF) model.

The Sanchez-Lacombe model has analytical expressions [1,2] for the classical critical properties, but the RLF model cannot obtain analytical expressions. Since it is hard to straightly obtain the classical critical properties for the RLF model, a method of getting them is required. As shown in Fig. 1, minimum of $(\partial P/\partial\rho)$, $(\partial P/\partial\rho)|_{min}$ is less than zero for $T<T_{oc}$ and $(\partial P/\partial\rho)|_{min}$ is greater than zero for $T>T_{oc}$. Therefore, $(\partial P/\partial\rho)|_{min}$ is zero at the classical critical temperature and volume:

$$\left.\frac{\partial P}{\partial \rho}\right|_{min} = 0 \ \text{ at } \ T = T_{oc},\ v = v_{oc} \tag{11}$$

$$P_{oc} = P^*\tilde{T}_{oc}\left[-\ln(1-\tilde{\rho}_{oc}) + \frac{z}{2}\ln\left[1+\left(\frac{q}{r}-1\right)\tilde{\rho}_{oc}\right] - \frac{\theta_{oc}}{\tilde{T}}\right] \tag{12}$$

$$\text{where } \theta_{oc} = \frac{(q/r)\tilde{\rho}_{oc}}{1+(q/r-1)\tilde{\rho}_{oc}} \tag{13}$$

CROSSOVER RANDOM LATTICE FLUID MODEL

To derive the crossover random lattice fluid (xRLF) model, let us follow the method developed by Kiselev [7,8].

First, it is required to recast the classical expression for Helmholtz free energy into dimensionless form as follows:

$$\overline{A}(T,v) = \Delta\overline{A}(\Delta T, \Delta v) + \overline{A}_{bg}(\Delta T, \Delta v) \tag{14}$$

where the critical part of the Helmholtz free energy

$$\Delta\overline{A}(\Delta T, \Delta v) = \overline{A}^r(\Delta T, \Delta v) - \overline{A}^r(\Delta T, 0) - \ln(\Delta v + 1) + \Delta v\overline{P}_0(\Delta T) \tag{15}$$

and the background contribution is given by

$$\overline{A}_{bg}(\Delta T, \Delta v) = -\Delta v\overline{P}_0(T) + \overline{A}_0^r(T) + \overline{A}_0(T) - \ln v_{oc} \tag{16}$$

Here $\Delta T = T/T_{oc} - 1$, $\Delta v = v/v_{oc} - 1$ are dimensionless distances from the classical temperature T_{oc} and molar volume v_{oc} respectively, in Eqs. (14)-(16). $\overline{P}_0(T) = P(T, v_{oc})/RT$ is the dimensionless pressure, $\overline{A}_0^r(T) = \overline{A}^r(T, v_{oc})$ is the dimensionless residual part of the Helmholtz free energy along the critical isochore $v=v_{oc}$. Then replace the classical dimensional temperature ΔT and Δv in the singular or critical term with renormalized values.

Table 1. System-dependent molecular parameters for the crossover random lattice fluid (xRLF) EOS

Components	Crossover parameters			Crossover parameters		
	T^*/K	P^*/MPa	ρ^*/g cm^{-3}	Gi	v_1	d_1
Methane	266.73	81.21	0.241	0.2387	0.0007	−0.2190
Ethane	385.75	140.83	0.297	0.1773	0.0008	0.0129
Propane	462.69	159.76	0.430	0.1156	0.0010	0.0100
n-Butane	524.31	140.83	0.420	0.1401	0.0008	0.0129
n-Pentane	452.83	204.75	0.422	0.3381	0.0016	0.8393
n-Hexane	482.42	332.70	0.566	0.1249	0.0014	2.0637
Carbon dioxide	273.51	1281.03	1.429	0.0967	0.0018	8.5411

Table 2. The deviations of vapor pressure and saturated liquid density with the classical random lattice fluid (RLF), crossover random lattice fluid (xRLF) and crossover Sanchez-Lacombe (xLF) EOS

Components	AAD % of $P^{sat,a}$			AAD % of ρ^b			T range/K
	RLF EOS	xRLF EOS	xLF EOS	RLF EOS	xRLF EOS	xLF EOS	
Methane	2.63	1.88	1.95	5.43	0.37	0.46	155 to 190
Ethane	1.15	1.81	1.92	2.84	0.21	0.24	240 to 305
Propane	1.38	1.16	1.29	2.91	0.33	0.42	310 to 369
n-Butane	2.41	1.35	1.98	5.43	0.68	0.75	355 to 425
n-Pentane	1.04	0.56	0.71	4.87	0.52	0.60	400 to 469
n-Hexane	3.48	1.34	1.99	3.17	0.33	0.46	440 to 506
Carbon dioxide	1.12	0.97	1.01	7.95	0.75	0.86	240 to 304

^{a}AAD % of $P^{sat}=(1/n)\cdot\left(\sum_i^n\left|(P_{i,exp}^{Sat.}-P_{i,calc}^{Sat.})/P_{i,exp}^{Sat.}\right|\right)\times 100$

^{b}AAD % of $\rho=(1/n)\cdot\left(\sum_i^n\left|(\rho_{i,exp}^{Sat.}-\rho_{i,calc}^{Sat.})/\rho_{i,exp}^{Sat.}\right|\right)\times 100$

$$\tau=\tau Y^{\frac{\alpha}{2\Delta_1}}+(1+\tau)\Delta\tau_c Y^{\frac{2(2-\alpha)}{3\Delta_1}} \tag{17}$$

$$\bar{\varphi}=\varphi Y^{\frac{(\gamma-2\beta)}{4\Delta_1}}+(1+\varphi)\Delta v_c Y^{\frac{2(2-\alpha)}{2\Delta_1}} \tag{18}$$

where α=0.11, β=0.325, γ=2−2β−α=1.24 and Δ_1=0.51 are universal non-classical critical exponents [14]. $\tau=(T/T_c)-1$ is a dimensionless deviation of the temperature from the real critical temperature τ_c, $\varphi=(v/v_c)-1$ is a dimensionless deviation of the molar volume from the real critical molar volume v_c, and $\Delta\tau_c=(T_c/T_{oc})-1$, $\Delta v_c=(v_c/v_{oc})-1$.

The crossover function Y can be written in the parametric form

$$Y(q)=\left(\frac{q}{1+q}\right)^{2\Delta_1} \tag{19}$$

where q is a renormalized distance to the critical point and can be found from the solution of the crossover sine-model (SM) [15].

$$\left(q^2-\frac{\tau}{Gi}\right)\left[1-\frac{p^2}{4b^2}\left(1-\frac{\tau}{q^2Gi}\right)\right]=b^2\left\{\frac{\Delta\eta[1+v_1\exp(-10\Delta\eta)]+d_1\tau}{m_0Gi^{\beta}}\right\}Y^{\frac{(1-2\beta)}{\Delta_1}} \tag{20}$$

where b^2 is the universal linear-model parameter and p^2 the universal sine-model parameters, $p^2=b^2=1.359$. Gi is the Ginzburg number for the fluid of interest [16] and we set m_0=1 in this study. v_1, d_1, and Gi are the system-dependent parameters.

Finally, the crossover form of the Helmholtz free energy can be written as

$$\bar{A}(T,v)=\Delta\bar{A}(\bar{\tau},\bar{\varphi})-\Delta v\bar{P}_0(T)+\bar{A}_0'(T)+\bar{A}_0(T)-\ln v_{oc} \tag{21}$$

where the critical part $\Delta\bar{A}$ is given by

$$\Delta\bar{A}(\bar{\tau},\bar{\varphi})=\bar{A}'(\bar{\tau},\bar{\varphi})-\bar{A}'(\bar{\tau},0)-\ln(\bar{\varphi}+1)+\bar{\varphi}\bar{P}_0(\bar{\tau},0) \tag{22}$$

The final xRLF EOS and chemical potential of pure component read

$$P(T,v)=-\left(\frac{\partial A}{\partial v}\right)_T=\frac{RT}{v_{oc}}\left[-\frac{v_{oc}}{v_c}\left(\frac{\partial\Delta\bar{A}(\bar{\tau},\bar{\varphi})}{\partial\varphi}\right)_T+\bar{P}_0(T)\right] \tag{23}$$

Table 3. The deviations of properties with the classical random lattice fluid (RLF), crossover random lattice fluid (xRLF) and crossover Sanchez-Lacombe (xLF) EOS

Components	AAD % of P^a			T range/K
	RLF EOS	xRLF EOS	xLF EOS	
Methane	65.37	1.64	1.84	150 to 230
Ethane	11.98	1.38	1.45	260 to340
Propane	19.42	1.54	1.87	320 to 420
n-Butane	51.53	1.69	1.78	380 to 480
n-Pentane	32.39	1.23	1.34	440 to 540
n-Hexane	29.63	1.25	1.46	460 to 560
Carbon dioxide	19.84	1.01	1.07	260 to 340

^{a}AAD % of $P^{sat}=(1/n)\cdot\left(\sum_i^n\left|(P_{i,exp}^{\cdot}-P_{i,cal}^{\cdot})/P_{i,exp}^{\cdot}\right|\right)\times 100$

$$\frac{\mu}{RT} = \frac{a}{RT} + Z \tag{24}$$

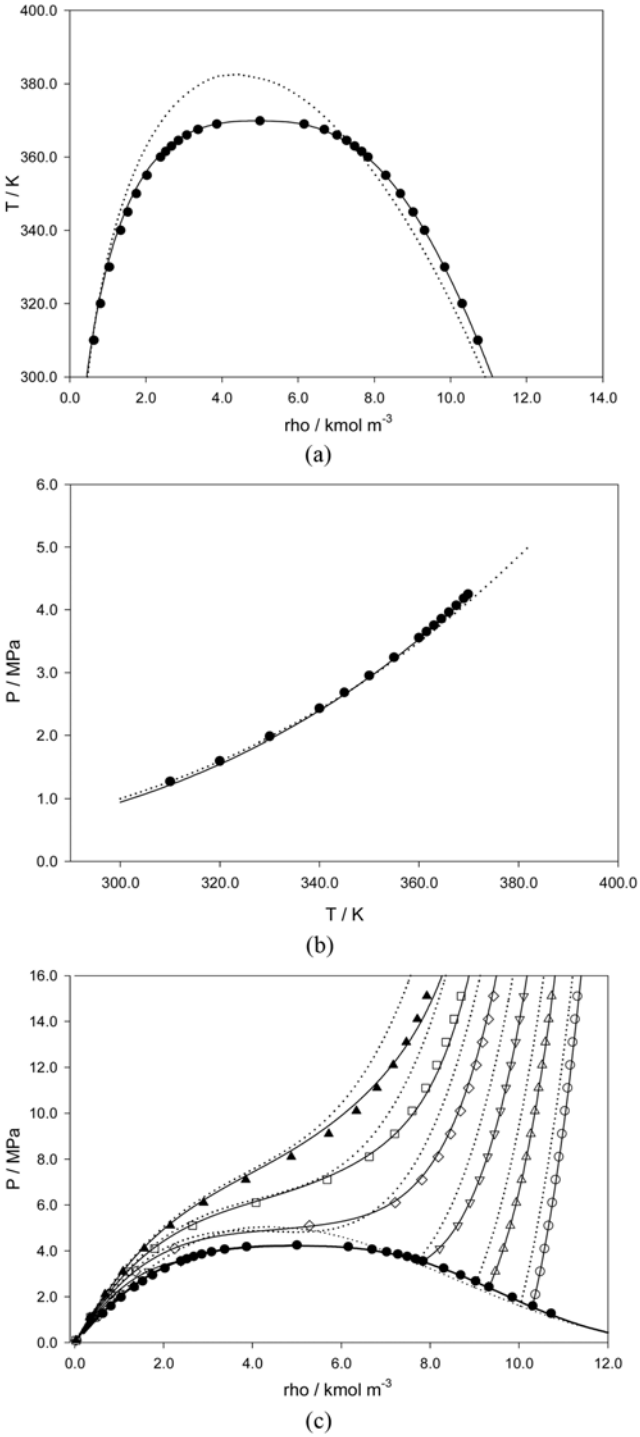

Fig. 2. (a) The saturated density data for propane with predictions of the RLF EOS (dotted curves), the xRLF EOS (solid curves). ●, Experimental saturated density. (b) The vapor pressure data for propane with predictions of the RLF EOS (dotted curves), the xRLF EOS (solid curves). ●, Experimental vapor pressure. (c) The data for propane with predictions of the LF EOS (dotted curves), the xLF EOS (solid curves). ●, VLE data; ○, 320 K; △, 340 K; ▽, 360 K; ◇, 380 K; □, 400 K; ▲, 420 K.

RESULTS AND DISCUSSION

To demonstrate the accuracy of the xRLF model, the xRLF was compared with the classical RLF model. The xRLF model for pure

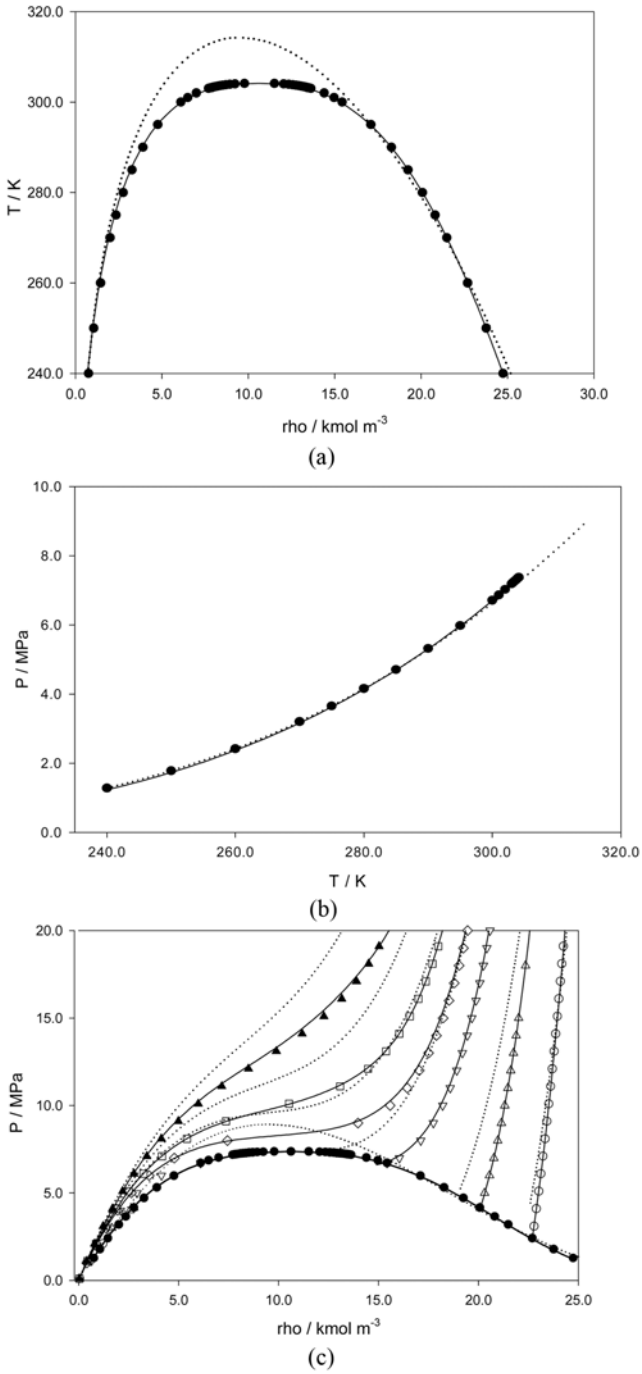

Fig. 3. (a) The saturated density data for carbon dioxide with predictions of RLF EOS (dotted curves), the xRLF EOS (solid curves). ●, Experimental saturated density. (b) The vapor pressure data for carbon dioxide with predictions of the RLF EOS (dotted curves), the xRLF EOS (solid curves). ●, Experimental vapor pressure. (c) The data for carbon dioxide with predictions of the RLF EOS (dotted curves), the xRLF EOS (solid curves). ●, VLE data; ○, 260 K; △, 280 K; ▽, 300 K; ◇, 310 K; □, 320 K; ▲, 340 K.

fluids contains three sets of system-dependent parameters: (1) the classical parameters, T^*, P^* and ρ^*; (2) the crossover parameters, Gi, v_1 and d_1 (3) the critical shifts of fluids, $\Delta\tau_c$ and Δv_c. Since the real parameters T_c and v_c for one-component fluids are usually known, $\Delta\tau_c$ and Δv_c are known too. Therefore, the xRLF EOS contains six adjustable parameters that can be found by fitting the xRLF EOS to their experimental saturated vapor pressure and saturated density data for eight pure systems (carbon dioxide, normal alkanes from methane to hexane). All experimental data are obtained from the Korea thermophysical properties databank (KDB) [17]. The values of six system-dependent parameters for eight pure fluids in the xRLF EOS are listed in Table 1.

The deviations of the VLE and $P\rho T$ properties calculated with the classical RLF, xRLF and crossover Sanchez-Lacombe (xLF) EOS [9] are listed in Tables 2 and 3. For all compounds, the xRLF EOS presented more excellent agreement with experimental data than the classical RLF EOS. The xRLF EOS showed slightly better results than the crossover Sanchez-Lacombe EOS. It is explained that near the critical point, the effect of density fluctuations would be more important than that of finite coordination number. In Figs. 2 and 3, the xRLF prediction for the vapor pressure and saturated density curve of propane and carbon dioxide is presented and compared with that from the classical RLF approach and experimental data. From the figure, the over-prediction of the critical point is apparently seen with the classical RLF approach, while excellent agreement is shown with the xRLF EOS. Therefore, the xRLF EOS could achieve excellent agreement with experimental data both in the critical region and at low temperatures and pressures.

CONCLUSION

A crossover random lattice fluid (xRLF) EOS is presented near and far from the critical region, which incorporates the scaling laws valid asymptotically close to the critical point while reducing to the original classical RLF EOS far from the critical point. With the incorporation of a crossover function into the RLF EOS, the non-analytical, singular behavior of fluids in the critical region and the accurate description of the whole phase diagram could be reproduced. The results presented here for selected hydrocarbons and carbon dioxide are seen to be in excellent agreement with experimental data both near to and far from the critical region. In next study, this crossover approach will be extended to more rigorous quasi-chemical [18] or multi-fluid [19,20] nonrandom lattice fluid model.

NOMENCLATURE

a : Helmholtz free energy per mole [J mol^{-1}]
A : Helmholtz free energy [J]
$\bar{A}$: dimensionless Helmholtz free energy
b^2 : universal linear-model parameter
d_1 : rectilinear diameter amplitude
Gi : Ginzburg number
P : pressure
R : R gas constant
r : number of segments per molecule
T : temperature
V : volume
v : molar volume
v^* : close packed volume of a mer
z : lattice coordination number
Z : compressibility factor

Greek Letters

ε^* : molecular energy parameter
ρ : molar density
ρ^* : close packed molar density
φ : order parameter
$\bar{\varphi}$: renormalized order parameter
θ : surface area fraction
τ : reduced temperature difference
$\bar{\tau}$: renormalized temperature difference

Subscript

id : ideal gas state
r : residual properties

Superscript

0 : classical
c : critical
~ : reduced properties
* : characteristic properties

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