

A crossover multi-fluid nonrandom lattice fluid model for pure hydrocarbons and carbon dioxide near to and far from the critical region

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Abstract—The multi-fluid nonrandom lattice fluid model with the local composition concept is capable of describing thermodynamic properties for complex systems, but this model cannot represent the singular behavior of fluids near the critical region. In this research, the multi-fluid nonrandom lattice fluid model for pure fluids is combined with a crossover theory to obtain a crossover multi-fluid nonrandom lattice fluid model which incorporates the critical scaling laws valid asymptotically close to the critical point and reduces to the original classical multi-fluid nonrandom model far from the critical point. The crossover multi-fluid nonrandom lattice fluid model shows a great improvement in prediction of the thermodynamic properties of pure compounds near the critical region.

Key words: Crossover, Multi-fluid, Nonrandom, Lattice Model, Critical Region

INTRODUCTION

Accurate predictions of the phase equilibria and thermodynamic properties are essential in a chemical process and product in various industries over a wide range of temperature and pressure. Because of their central importance to the practice of chemical engineering, many thermodynamic models have been developed, based in some cases on theory and frequently on empiricism. As applied in normal conditions far from the critical regions, classical lattice models can accurately calculate and predict physical properties. However, these models [1-5] fail to satisfactorily reproduce physical properties near the critical region where thermodynamic properties exhibit a singular behavior [6]. This reason is that the classical lattice models are based on mean field approximation, which neglects density fluctuation near the critical regions. Near the critical point where the compressibility is large, density fluctuations extend over macroscopic dimension. Therefore, the instantaneous picture of a fluid near the critical point is an inhomogeneous state with high and low density regions extending over the correlation length. Because these fluctuations extend over inter-particle distances, the phase behavior is determined by the size and nature of the fluctuations rather than by the particular features of the molecular interactions. In the vicinity near the critical point, the correct phase behavior is expressed by the critical exponents, i.e., in many experiments, it has been found that all properties, such as pressure, volume, heat capacity, and isothermal compressibility, show universal behavior and are expressed by identical exponents for all systems.

Many efforts have been made to overcome the deficiency of classical thermodynamic models in describing physical properties near the critical point. A crossover theory was used to combine the advantages of each approach by connecting these conceptually different theories. Kiselev et al. [7,8] proposed a simple crossover theory and

successfully calculated the thermodynamic properties of fluids near to and far from the critical region. In the development and application of the thermodynamic models using Kiselev's method, obtaining appropriate values in terms of mean renormalized distances from the critical point, is the main item to the development of a successful model. In the former researches [9-15], the present authors presented the crossover cubic equation of state, the Sanchez-Lacombe lattice fluid model and the crossover random lattice fluid model that combine the crossover scale laws valid asymptotically close to the critical point and reduce to the original thermodynamic models far from the critical point. The Sanchez-Lacombe lattice fluid model uses the full Guggenheim combinatory but assumes that the nonrandom contribution is negligible and that this model takes up the large coordination number limit known as the Flory approximation. The random lattice fluid model also has negligible nonrandom contribution.

In this study, the multi-fluid nonrandom lattice fluid model with local composition concept was used and an expression for the critical properties of this model also was presented. We have combined this model with the crossover theory to obtain the crossover multi-fluid nonrandom lattice fluid model and to calculate the thermodynamic properties near to and far from the critical point.

CROSSOVER MULTI-FLUID NONRANDOM LATTICE FLUID MODEL

The multi-fluid nonrandom lattice model (MF-NLF) lattice model was developed on the two-liquid approximation of the lattice hole theory [16-18] and extended to complex systems containing polymers [19], associating fluids [20] and water [21]. However, the MF-NLF model has strong temperature dependence of energy parameters and segment numbers of pure systems thus, empirical correlations as functions of temperature were adopted for reliable and convenient use in engineering practices. The present authors [4,5] recently presented a new version of multi-fluid nonrandom lattice fluid (MLF)

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model with no temperature-dependent molecular parameters and obtained the expression of fugacity coefficients for phase equilibrium calculations. This MLF model is capable of describing thermodynamic properties for complex systems containing associating fluids [22] and surfactants [23]. However, this classical MLF model is not applicable near the critical region due to mean-field approximation.

In this study, the MLF model with local composition concept was chosen as a reference lattice fluid model and was represented as follows:

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

Here, all the quantities with the tilde ($\sim$) denote the reduced variables defined by

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

where the reducing parameters are defined by

$$P^* v_i^* = kT^* = \frac{z}{2} \varepsilon_M \quad (3)$$

and ε_M is defined by

$$\varepsilon_M = \frac{1}{\beta \theta^2} \left[\sum_{i=1}^1 \theta_i \left(1 - \frac{\tau_{0i}}{\sum_{k=0}^1 \theta_k \tau_{ki}} \right) \right] \quad (4)$$

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

$$\theta = \frac{N_i q_i}{N_q} = \frac{(q/r)\tilde{\rho}}{1 + (q/r-1)\tilde{\rho}} = 1 - \theta_0 \quad (5)$$

Here r is segment number, q is surface area parameter and the nonrandomness factor τ_{ji} is defined as,

$$\tau_{ji} = \exp[\beta(\varepsilon_{ji} - \varepsilon_{ii})] \quad (6)$$

Let us set coordination number, $z=10$, as used in lattice fluid theories of the same genre [24,25].

The MLF model 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:

$$A^r(T, v) = - \int_{\infty}^v \left(P - \frac{nRT}{V} \right) dV = nRT \left[\left(\frac{1}{\tilde{\rho}} - 1 \right) \ln(1-\tilde{\rho}) \right] - RT \left[\frac{znr}{2\tilde{\rho}} + n(1-r) \right] \ln \left(1 + \left(\frac{q}{r} - 1 \right) \tilde{\rho} \right) + nRT - \frac{nqRT\theta}{\tilde{T}} \quad (7)$$

The molar Helmholtz free energy can be written as:

$$a(T, v) = a^r(T, v) + a^{id}(T, v) \quad (8)$$

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

$$a^{id}(T, v) = -RT \ln v + a_0(T) \quad (9)$$

In Eq. (9), $a_0(T)$ is the temperature-dependent part of the Helmholtz free energy for ideal gas.

The classical expression for the Helmholtz free energy $\bar{A}(T, v)$

was rewritten in the dimensionless form as follows:

$$\bar{A}(T, v) = \frac{a(T, v)}{RT} = \bar{A}^r(T, v) - \ln v + \bar{A}_0(T) \quad (10)$$

$$\bar{A}^r(T, v) = r \left[\left(\frac{1}{\tilde{\rho}} - 1 \right) \ln(1-\tilde{\rho}) \right] - \left[\frac{zr}{2\tilde{\rho}} + (1-r) \right] \ln \left(1 + \left(\frac{q}{r} - 1 \right) \tilde{\rho} \right) + 1 - \frac{q\theta}{\tilde{T}} \quad (11)$$

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

$$\left(\frac{\partial P}{\partial \rho} \right)_{T_{oc}} = \left(\frac{\partial^2 P}{\partial \rho^2} \right)_{T_{oc}} = 0 \quad (12)$$

Since it is hard to directly obtain the classical critical properties for the MLF model, a method of getting them is required as follows [15]:

$$\left. \frac{\partial P}{\partial \rho} \right|_{T_{oc}, v_{oc}} = 0 \quad \text{at } T = T_{oc}, \quad v = v_{oc} \quad (13)$$

$$P_{oc} = P^* \tilde{T}_{oc} \left[-\ln(1-\tilde{\rho}_{oc}) + \frac{z}{2} \ln \left[1 + \left(\frac{q}{r} - 1 \right) \tilde{\rho}_{oc} \right] - \frac{\theta_{oc}}{\tilde{T}} \right] \quad (14)$$

$$\text{where } \theta_{oc} = \frac{(q/r)\tilde{\rho}_{oc}}{1 + (q/r-1)\tilde{\rho}_{oc}} \quad (15)$$

To derive the crossover multi-fluid nonrandom lattice fluid (xMLF) model, we need to recast the classical expression for Helmholtz free energy into dimensionless form as follows:

$$\bar{A}(T, v) = \Delta \bar{A}(\Delta T, \Delta v) + \bar{A}_{bg}(\Delta T, \Delta v) = \bar{A}^r(\Delta T, \Delta v) - \bar{A}^r(\Delta T, 0) - \ln(\Delta v + 1) + \Delta v \bar{P}_0(\Delta T) - \Delta v \bar{P}_0(T) + \bar{A}_0^r(T) + \bar{A}_0(T) - \ln v_{oc} \quad (16)$$

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

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

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

where $\alpha=0.11$, $\beta=0.325$, $\gamma=2-2\beta-\alpha=1.24$ and $\Delta_1=0.51$ are universal non-classical critical exponent [26]. $\tau=(T/T_c)-1$ is a dimensionless deviation of the temperature from the real critical temperature T_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

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

where q is a renormalized distance to the critical point and can be found from the solution of the crossover sine-model (SM) [27].

$$\left(q^2 - \frac{\tau}{Gi} \right) \left[1 - \frac{p^2}{4b^2} \left(1 - \frac{\tau}{q^2 Gi} \right) \right]$$

Table 1. Molecular parameters for the crossover multi-fluid nonrandom lattice fluid (xMLF) EOS

Components	Crossover parameters			Crossover parameters		
	T*/K	P*/MPa	$\rho^*/\text{g cm}^{-3}$	Gi	v_1	d_1
Methane	266.65	81.17	0.239	0.2416	0.0006	-0.2181
Ethane	385.48	141.05	0.303	0.1781	0.0007	0.0131
Propane	461.95	160.14	0.428	0.1209	0.0009	0.0095
n-Butane	522.97	139.92	0.429	0.1396	0.0009	0.0118
n-Pentane	451.57	206.15	0.431	0.3424	0.0015	0.8408
n-Hexane	481.87	331.54	0.563	0.1252	0.0016	2.1126
Carbon dioxide	273.17	1279.92	1.432	0.1058	0.0021	8.5284

Table 2. Calculated deviations of saturated properties with the MLF, the xMLF and the xLF model

Components	AADP ^{sat, a}			AADP ^b			T range/K
	MLF	xMLF	xLF	MLF	xMLF	xLF	
Methane	1.99	0.94	1.95	4.81	0.26	0.46	155 to 190
Ethane	1.85	0.97	1.92	2.17	0.17	0.24	240 to 305
Propane	1.37	0.87	1.29	2.36	0.24	0.42	310 to 369
n-Butane	2.05	0.96	1.98	4.58	0.35	0.75	355 to 425
n-Pentane	1.03	0.46	0.71	4.26	0.32	0.60	400 to 469
n-Hexane	2.16	0.93	1.99	2.64	0.25	0.46	440 to 506
Carbon dioxide	1.10	0.69	1.01	6.57	0.61	0.86	240 to 304

$$^a \text{AADP}^{\text{sat}} = (1/n) \cdot \left(\sum_i^n |(P_{i,\text{exp}}^{\text{sat}} - P_{i,\text{calc}}^{\text{sat}})/P_{i,\text{exp}}^{\text{sat}}| \right) \times 100$$

$$^b \text{AADP}^{\rho} = (1/n) \cdot \left(\sum_i^n |(\rho_{i,\text{exp}}^{\text{sat}} - \rho_{i,\text{calc}}^{\text{sat}})/\rho_{i,\text{exp}}^{\text{sat}}| \right) \times 100$$

$$= b^2 \left\{ \frac{\Delta \eta [1 + v_1 \exp(-10 \Delta \eta)] + d_1 \tau}{m_0 G_i^{\beta}} \right\}^2 Y^{\frac{(1-2\beta)}{\Delta_1}} \quad (20)$$

where b^2 is the universal linear-model parameter and p^2 the universal sine-model parameters, $p^2 = b^2 = 1.359$. G_i is the Ginzburg number for the fluid of interest [28] and we set $m_0 = 1$ in this study. v_1 , d_1 , and G_i are the system-dependent parameters.

The crossover form of the Helmholtz free energy can be written as

$$\bar{A}(T, v) = \Delta \bar{A}(\bar{\tau}, \bar{\varphi}) - \Delta v \bar{P}_0(T) + \bar{A}_0(T) + \bar{A}_0(T) - \ln v_{oc} \quad (21)$$

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

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

The xMLF model can be obtained by differentiation of Eq. (21) with respect to volume

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

and chemical potential of pure component for phase equilibrium calculation is represented as follows:

$$\frac{\mu}{RT} = \frac{a}{RT} + Z \quad (24)$$

where Z is the compressibility factor.

As far away from the critical point ($q \rightarrow \infty$), the crossover function $Y \rightarrow 1$, $\tau \rightarrow \Delta T$ and $\varphi \rightarrow \Delta v$, and Eq. (21) is reduced to the clas-

sical Helmholtz free energy Eq. (10). Meanwhile, as asymptotically close to the critical point ($q \rightarrow 0$), the crossover function $Y \rightarrow q^{2\Delta_1}$ and it renormalizes ΔT and Δv in accordance with Eqs. (17) and (18), so giving the correct non-analytical asymptotic behavior of real fluids in the critical region.

RESULTS AND DISCUSSION

The xMLF model for pure fluids contains three sets of system-dependent parameters: (1) the classical parameters, T^* , P^* and ρ^* ; (2) the crossover parameters, G_i , v_1 and d_1 (3) the critical shifts of

Table 3. The deviations of $P\rho T$ properties with the MLF, the xMLF and the xLF model

Components	AADP ^a			T range/K
	MLF	xMLF	xLF	
Methane	57.94	0.96	1.84	150 to 230
Ethane	10.16	0.98	1.45	260 to 340
Propane	15.67	1.01	1.87	320 to 420
n-Butane	45.67	1.12	1.78	380 to 480
n-Pentane	31.08	0.94	1.34	440 to 540
n-Hexane	22.84	0.98	1.46	460 to 560
Carbon dioxide	15.84	0.93	1.07	260 to 340

$$^a \text{AADP} = (1/n) \cdot \left(\sum_i^n |(P_{i,\text{exp}} - P_{i,\text{calc}})/P_{i,\text{exp}}| \right) \times 100$$

fluids, $\Delta\tau_c$ and Δv_c . Because the real parameters T_c and v_c for pure fluids are usually known, $\Delta\tau_c$ and Δv_c are known too. Thus, the xMLF model contains six adjustable parameters. These parameters could be obtained by fitting the xMLF EOS to their experimental vapor pressure, saturated density and $P\rho T$ data for pure fluids. All experi-

mental data are obtained from the Korea thermophysical properties Databank (KDB) [29]. Six molecular parameters for pure fluids in the xMLF model are given in Table 1.

To test the accuracy of the xMLF model, the xMLF was compared with the classical MLF model and the crossover Sanchez-Lacombe (xLF) model [10]. The deviations of the VLE (vapor liquid

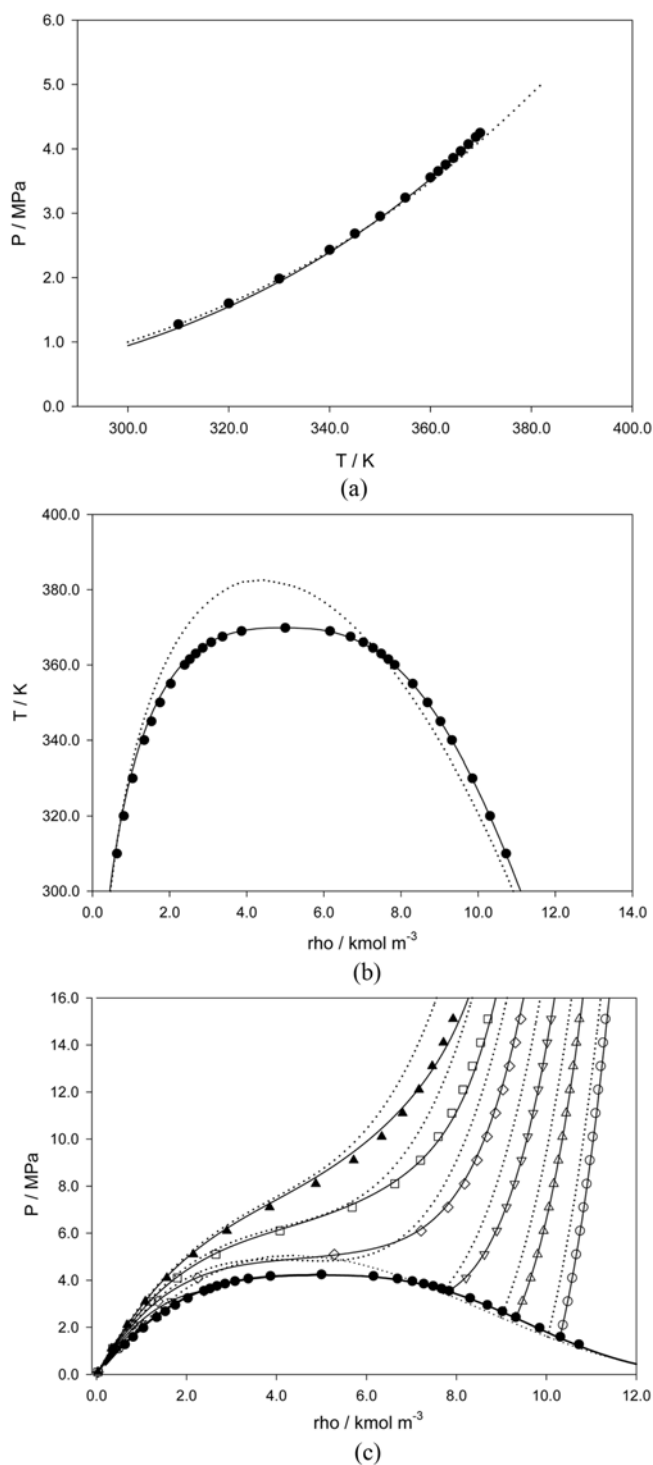


Fig. 1. Plot of thermodynamic properties with predictions of MLF EOS (dotted curves), the xMLF EOS (solid curves) for propane. (a) vapor pressure, (b) saturated density, (c) $P\rho T$: ●, saturated data; ○, 320 K; △, 340 K; ▽, 360 K; ◇, 380 K; □, 400 K; ▲, 420 K.

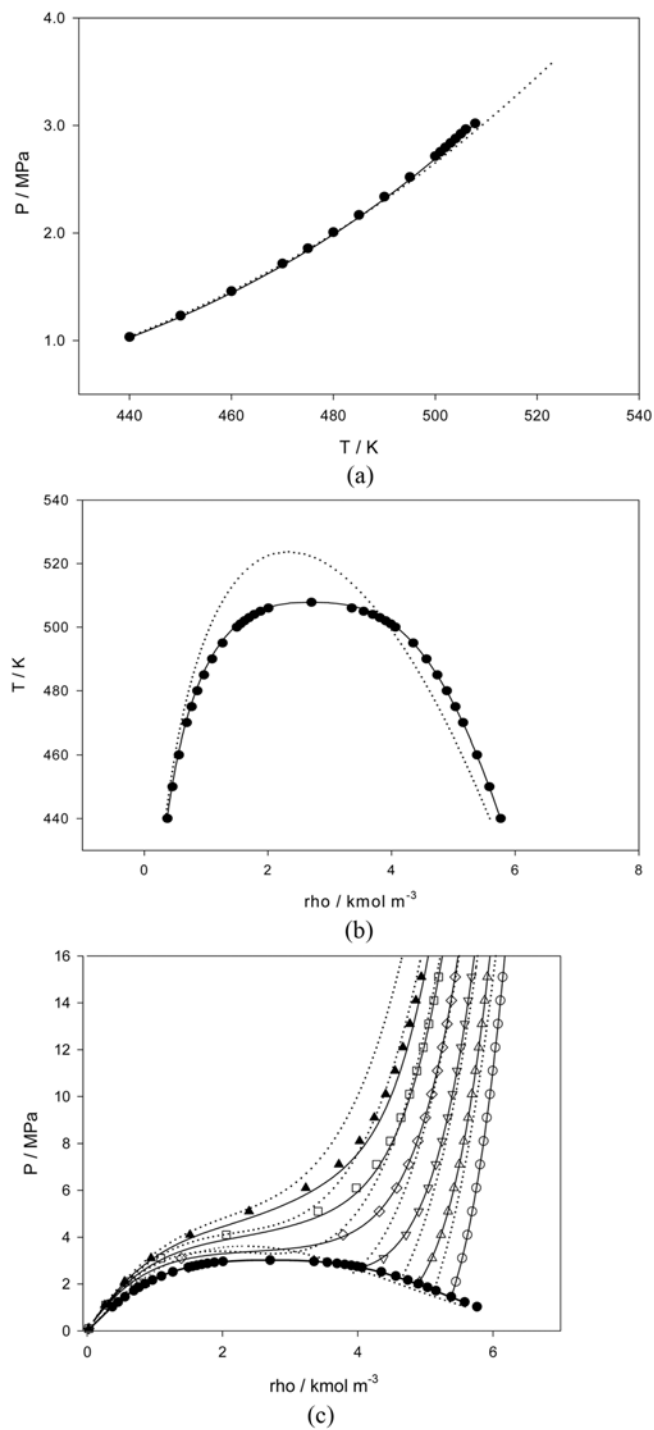


Fig. 2. Plot of thermodynamic properties with predictions of MLF EOS (dotted curves), the xMLF EOS (solid curves) for n-hexane. (a) vapor pressure, (b) saturated density, (c) $P\rho T$: ●, saturated data; ○, 460 K; △, 480 K; ▽, 500 K; ◇, 520 K; □, 540 K; ▲, 560 K.

equilibrium) and $P\rho T$ properties for pure fluids calculated with the classical MLF, xMLF and xLF model are listed in Tables 2 and 3. For all compounds, the xMLF model showed more great agreement with experimental data than the classical MLF model. The xMLF model, also, presented better results than the crossover Sanchez-Lacombe model. It is explained that the local composition concept of the xMLF model could be more important far from the critical point than near the critical region. In Figs. 1 and 2, the xMLF prediction for VLE and $P\rho T$ properties of propane and n-hexane are shown and compared with that from the classical MLF model and experimental data. From these figures, the classical MLF model showed apparently the over-prediction of the critical pressure and temperature, while the xMLF model could achieve excellent agreement with experimental data both near and far from the critical region. The xMLF model will be extended to second-order thermodynamic properties, mixture VLE properties and solid solubility in supercritical fluids in next study.

CONCLUSION

A crossover multi-fluid nonrandom lattice fluid for pure fluids is presented. The multi-fluid nonrandom lattice fluid model with local composition concept is combined with a crossover theory which incorporates the critical scaling laws valid asymptotically near the critical point and reduces to the original classical multi-fluid nonrandom model far from the critical region. The crossover multi-fluid nonrandom lattice fluid model reproduces thermodynamic properties of fluids in a global region including near to and far from the critical region and shows greater improvements than the classical multi-fluid nonrandom model and the crossover Sanchez-Lacombe model.

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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_i	: rectilinear diameter amplitude
G_i	: Ginzburg number
P	: pressure
q	: surface area parameter
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
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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
$\sim$	: reduced properties
*	: characteristic properties

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