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신문삼, 이용진, 장성현, 김화용*
서울대학교
(hwayongk@snu.ac.kr*)

A Crossover Quasi-Chemical Lattice Fluid Model from Singular Critical to Regular Classical Thermodynamic Behavior of Fluids

Moon Sam Shin, Yongjin Lee, Sung-hyun Chang, Hwayong Kim*
School of Chemical & Biological Engineering, Seoul National University
(hwayongk@snu.ac.kr*)

1. Introduction

The classical lattice models [1-3] have been successfully applied to describe the phase equilibrium of wide range industrially important fluids, such as alkanes, polymers and associating fluids. However, the accuracy of the lattice fluid models is limited to the region of the phase diagram away from the critical region due to mean-field approximation. For example, the classical lattice fluid model has an over-prediction of the critical point, as illustrated by dotted line in Figure 1. In order 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 rescaled lattice model, poor agreement is obtained for the coexisting liquid densities. Thus, in common with all classical equations of state, a single set of parameters in unable to describe accurately both the near critical and sub-critical regions. Hence, a better approach to describe the critical region with the lattice fluid model is needed.

In this study, we have combined the qausi-chemical lattice fluid equation of state with a crossover technique developed by Kiselev [5,6] to obtain the crossover lattice fluid equation of which incorporates the critical scaling laws valid asymptotically close to the critical point and reduces to the original classical equation of state far from the critical point

2. A crossover qausi-chemical lattice fluid EOS

The qausi-chemical lattice fluid (QLF) model [3] with no temperature dependence of pure parameters developed recently by the present authors and the QLF model was capable of describing thermodynamics properties of fluids in a wide range, except near the critical region. The QLF EOS was represented as follows;

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

where the reduced temperature, pressure, and density is defined by

$$\tilde{T}=\frac{T}{T^{*}}=\frac{RT}{\varepsilon^{*}} \qquad \tilde{P}=\frac{P}{P^{*}}=\frac{Pv^{*}}{\varepsilon^{*}} \qquad \tilde{\rho}=\frac{\rho}{\rho^{*}} \tag{2}$$

The QLF EOS has three molecular parameters; ε^*, v^*, and r, or equivalently the scale factors T^*, P^*, or ρ^*. The residual Helmholtz free energy $A^r(T,v)$ was obtained as follows;

$$A^r(T,v) = -\int_\infty^V \left(P - \frac{nRT}{V}\right) dV$$
$$= nrRT\left[(\frac{1}{\tilde{\rho}} - 1)\ln(1-\tilde{\rho})\right] - \left[\frac{z}{2}\frac{nrRT}{\tilde{\rho}} + nRT(1-r)\right]\ln(1+(\frac{q}{r}-1)\tilde{\rho}) + nRT - \frac{nRTq\theta}{\tilde{T}} \qquad (3)$$

The molar Helmholtz free energy can be written as:

$$a(T,v) = a^r(T,v) + a^{id}(T,v) \qquad (4)$$

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

$$a^{id}(T,v) = -RT\ln v + a_0(T) \qquad (5)$$

In Eq. (5), $a_o(T)$ is the temperature-dependent part of the Helmholtz free energy for ideal gas.

We rewrite the classical expression for the Helmholtz free energy $\bar{A}(T,v)$ in the dimensionless form as follows;

$$\bar{A}(T,v) = \frac{a(T,v)}{RT} = \bar{A}^r(T,v) - \ln v + \bar{A}_0(T) \qquad (6)$$

$$\bar{A}^r(T,v) = r\left[(\frac{1}{\tilde{\rho}} - 1)\ln(1-\tilde{\rho})\right] - \left[\frac{z}{2}\frac{r}{\tilde{\rho}} + (1-r)\right]\ln(1+(\frac{q}{r}-1)\tilde{\rho}) + 1 - \frac{q\theta}{\tilde{T}} \qquad (7)$$

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

$$\left(\frac{\partial P}{\partial v}\right)_{T_{oc}} = \left(\frac{\partial^2 P}{\partial v^2}\right)_{T_{oc}} = 0 \qquad (8)$$

In order to derive the crossover (xQLF) EOS, we need to recast the classical expression for Helmholtz free energy into dimensionless form as follows;

$$\bar{A}(T,v) = \Delta\bar{A}(\Delta T,\Delta v) + \bar{A}_{bg}(\Delta T,\Delta v) \qquad (9)$$

where the critical part of the Helmholtz free energy

$$\Delta\bar{A}(\Delta T,\Delta v) = \bar{A}^r(\Delta T,\Delta v) - \bar{A}^r(\Delta T,0) - \ln(\Delta v + 1) + \Delta v\bar{P}_0(\Delta T) \qquad (10)$$

and the background contribution is given by

$$\bar{A}_{bg}(\Delta T,\Delta v) = -\Delta v\bar{P}_0(T) + \bar{A}_0^r(T) + \bar{A}_0(T) - \ln v_{oc} \qquad (11)$$

In Eqs. (9-11), $\Delta T = T/T_{oc} - 1$, $\Delta v = v/v_{oc} - 1$ 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 $v = v_{oc}$.

We then replace the classical dimensional temperature ΔT and Δv in the singular or critical term with renormalized values.

$$\bar{\tau} = \tau Y^{-\frac{\alpha}{2\Delta_1}} + (1+\tau)\Delta\tau_c Y^{\frac{2(2-\alpha)}{3\Delta_1}} \qquad (12)$$

$$\bar{\varphi} = \varphi Y^{\frac{(\gamma-2\beta)}{4\Delta_1}} + (1+\varphi)\Delta v_c Y^{\frac{2(2-\alpha)}{2\Delta_1}} \qquad (13)$$

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. $\tau = (T/T_c) - 1$ 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

$$Y(q) = \left(\frac{q}{1+q}\right)^{2\Delta_1} \tag{14}$$

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

$$(q^2 - \frac{\tau}{Gi})[1 - \frac{p^2}{4b^2}(1 - \frac{\tau}{q^2 Gi})] = b^2\{\frac{\Delta\eta[1 + v_1\exp(-10\Delta\eta)] + d_1\tau}{m_0 Gi^{\beta}}\}^2 Y^{\frac{(1-2\beta)}{\Delta_1}} \tag{15}$$

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 and we set $m_0 = 1$ in this study. v_1, d_1, and Gi are the system-dependent parameters.

Finally, the crossover expression for the Helmholtz free energy can be written in the form

$$\overline{A}(T,v) = \Delta\overline{A}(\overline{\tau},\overline{\varphi}) - \Delta v\overline{P}_0(T) + \overline{A}_0^r(T) + \overline{A}_0(T) - \ln v_{oc} - K(\tau^2) \tag{16}$$

where, the critical part $\Delta\overline{A}$ is written as

$$\Delta\overline{A}(\overline{\tau},\overline{\varphi}) = \overline{A}^r(\overline{\tau},\overline{\varphi}) - \overline{A}^r(\overline{\tau},0) - \ln(\overline{\varphi}+1) + \overline{\varphi}\,\overline{P}_0(\overline{\tau},0) \tag{17}$$

$$K(\tau^2) = \frac{1}{2}a_{20}\tau^2(Y^{-\alpha/\Delta_1} - 1) + \frac{1}{2}a_{21}\tau^2(Y^{-(\alpha-\Delta_1)/\Delta_1} - 1) \tag{18}$$

The xLF EOS can be obtained by differentiation of Eq. (16) with respect to volume

$$P(T,v) = -\left(\frac{\partial A}{\partial v}\right)_T = \frac{RT}{v_{oc}}\left[-\frac{v_{oc}}{v_c}\left(\frac{\partial\Delta\overline{A}(\overline{\tau},\overline{\varphi})}{\partial\varphi}\right)_T + \overline{P}_0(T) + \frac{v_{oc}}{v_c}\left(\frac{\partial K(\tau^2)}{\partial\varphi}\right)_T\right] \tag{19}$$

The crossover function Y asymptotically close to the critical point renormalizes ΔT and Δv in accordance with Eqs. (12) and (13), so giving the correct non-analytical asymptotic behavior of real fluids in the critical region. Far away from the critical point the crossover function $Y \rightarrow 1$, $\tau \rightarrow \Delta T$ and $\varphi \rightarrow \Delta v$, and Eq. (16) is reduced to the classical Helmholtz free energy Eq. (9)

The second order is also calculated by the thermodynamic relations as follows;

$$C_v = -T(\frac{\partial^2 A}{\partial T^2})_v,\quad k_T^{-1} = \rho(\frac{\partial P}{\partial\rho})_T,\quad \alpha = k_T(\frac{\partial P}{\partial T})_v,\quad C_P = C_v + \frac{T\alpha^2}{k_T\rho},\quad w = \sqrt{\frac{C_P}{C_v}(\frac{\partial P}{\partial\rho})_T} \tag{20}$$

3. Results and Discussion

For one-component fluids, the xQLF EOS contains four 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; (4) kernel term parameters, a_{20} and a_{21} . 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. As a consequence, the xQLF EOS contains 8 adjustable parameters. We find these parameters for carbon dioxide by fitting the xQLF EOS to their experimental saturated vapor pressure and saturated density data. All experimental data are obtained from the NIST database [7].

Comparisons of the xQLF EOS with experimental data and the classical QLF EOS are shown in Figure 1 for carbon dioxide. From the figure we can see the over-prediction of the critical point with the QLF approach, compared to the excellent agreement obtained with the xQLF EOS. With the xQLF EOS we are able to achieve excellent agreement with experimental data both in the critical region and at low temperatures and pressures.

4. CONCLUSION

A crossover lattice fluid (xQLF) EOS is developed. The classical lattice fluid (QLF) EOS fails to reproduce the non-analytical, singular behavior of fluids in the critical region. Through the incorporation of a crossover function into the LF EOS, which exhibits classical behavior in the critical region rather than the non-analytical, singular behavior seen in real fluids we are able to provide an accurate description of the whole phase diagram using xLF EOS. The results presented here for selected carbon dioxide are seen to be in excellent agreement with experimental data both near to and far from the critical region.

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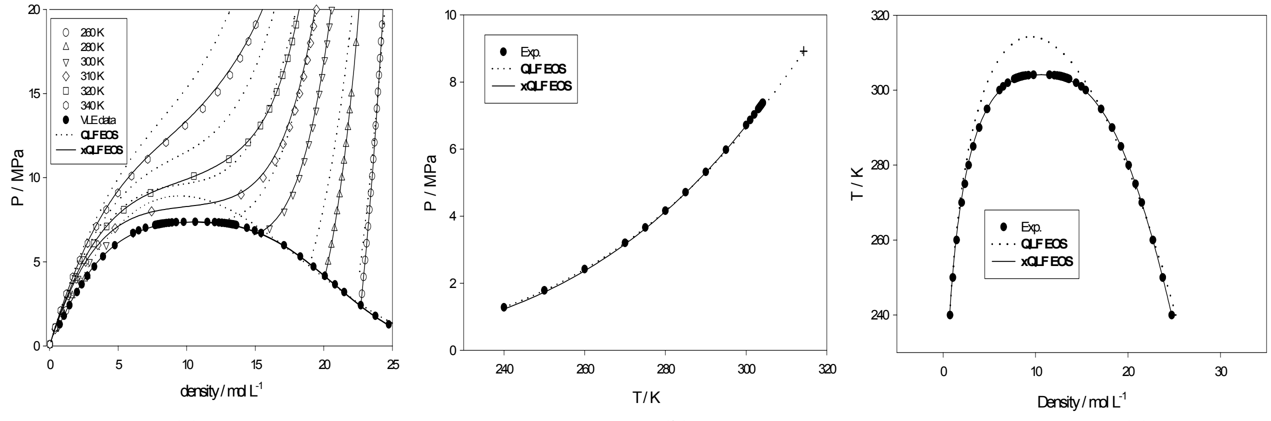

(a) (b) (c)

Figure 1. The $P\rho T$ data (a), saturated density data (b), vapor pressure data (c for carbon dioxide with predictions of the QLF and xQLF EOS.