

Application of the crossover lattice equation of state for fluid mixtures

Yongjin Lee^a, Moon Sam Shin^a, Byoungjo Ha^b, Hwayong Kim^{a,*}

^a School of Chemical and Biological Engineering and Institute of Chemical Processes, Seoul National University, Seoul 151-744, Republic of Korea

^b Eulji University, 212, Yangji-dong, Sujeong-Gu, Seongnam 461-713, Republic of Korea

Received 28 December 2007; received in revised form 25 January 2008; accepted 25 January 2008

Available online 2 February 2008

Abstract

In previous work, we developed the crossover lattice equation of state (xLF EOS) for pure fluids and the xLF EOS yielded the saturated vapour pressure and the density values with a much better accuracy than the classical LF EOS over a wide range. In this work, we extended xLF EOS to fluid mixtures. Classical composition-dependent mixing rules with only adjustable two binary interaction parameters same as the LF EOS are used. A comparison is made upon experimental data for fluids mixtures in the one- and two-phase regions. The xLF EOS shows more improved representations than the LF EOS, especially in the critical region.

© 2008 Elsevier Ltd. All rights reserved.

Keywords: Critical point; Crossover theory; Equation of state; Lattice fluid equation of state; Sanchez–Lacombe equation of state; Supercritical fluid

1. Introduction

Accurate predictions of the thermodynamic properties and phase behaviour of fluid mixtures are very important for chemical process and product design in various industries. Over decades, significant efforts have been made for the development of better thermodynamic models. The most of these classical models gave very accurate predictions of the thermodynamics properties of fluids over a wide range, but these classical models did not calculate them well near the critical region due to mean field approximation. In the critical region, phase behaviour of fluids can be expressed exactly by the universal critical exponents and many models based on those exponents had been developed. But they did not reproduce the ideal gas equation of state in the limit of zero density. To connect both of the conceptually different theories, the crossover theory has been studied. A simple theory proposed and improved by Kiselev [1] gave successful representations of the thermodynamic properties of fluids over a wide range including the ideal gas limit and the critical region. In previous study

[2], the lattice fluid equation of state (LF EOS) was combined with the crossover theory developed by Kiselev [1] to obtain the crossover lattice fluid equation of state 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. For various pure systems, the crossover lattice equation of state (xLF EOS) yielded the saturated data and the PVT data with a much better accuracy than the LF EOS.

In this work, we continue a study begun in our previous paper about the development of the xLF EOS and extend the xLF EOS to fluid mixtures. In Section 2, we describe the crossover equation of state for pure components and mixture systems. Comparisons with experimental data are presented in Section 3; and conclusions are drawn in Section 4.

2. Theory

In previous work, the Sanchez–Lacombe EOS [3,4] was chosen as a reference LF model and the crossover lattice equation of state was obtained. The LF EOS was derived from the configurational partition function according to statistical mechanics and was capable of describing thermodynamics properties of fluids in a wide range, except

* Corresponding author. Tel.: +82 2 888 7406; fax: +82 2 888 6695.
E-mail address: hwayongk@snu.ac.kr (H. Kim).

near the critical region. The LF EOS was represented as follows:

$$Z = r \frac{\tilde{P}}{\tilde{T}\tilde{\rho}} = r \left[-\frac{1}{\tilde{\rho}} \ln(1 - \tilde{\rho}) - \left(1 - \frac{1}{r}\right) - \frac{\tilde{\rho}}{\tilde{T}} \right], \quad (1)$$

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

$$\tilde{T} = \frac{T}{T^*} = \frac{RT}{\varepsilon^*}, \quad \tilde{P} = \frac{P}{P^*} = \frac{Pv^*}{\varepsilon^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*}. \quad (2)$$

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

In order to derive the crossover (xLF) EOS using the crossover theory, we followed the method developed by Kiselev [1].

Firstly, we need to recast the classical expression for Helmholtz energy into dimensionless form as follows:

$$\bar{A}(T, v) = \Delta\bar{A}(\Delta T, \Delta v) + \bar{A}_{bg}(\Delta T, \Delta v), \quad (3)$$

where the critical part of the Helmholtz free energy

$$\Delta\bar{A}(\Delta T, \Delta v) = \bar{A}^r(\Delta T, \Delta v) - \bar{A}^r(\Delta T, 0) - \ln(\Delta v + 1) + \Delta v \bar{P}_0(\Delta T), \quad (4)$$

and the background contribution are given by:

$$\bar{A}_{bg}(\Delta T, \Delta v) = -\Delta v \bar{P}_0(T) + \bar{A}_0^r(T) + \bar{A}_0(T) - \ln v_{oc}. \quad (5)$$

In equations (3)–(5), $\Delta T = T/T_{oc} - 1$, $\Delta v = v/v_{oc} - 1$ 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 energy along the critical isochore $v = v_{oc}$. Then the classical dimensional temperature ΔT and Δv in the singular or critical term is replaced with renormalized values. The

$$\bar{\tau} = \tau Y^{-\frac{\alpha}{2\Delta_1}} + (1 + \tau) \Delta\tau_c Y^{\frac{2(2-\alpha)}{3\Delta_1}}, \quad (6)$$

$$\bar{\varphi} = \varphi Y^{\frac{(\gamma-2\beta)}{4\Delta_1}} + (1 + \varphi) \Delta v_c Y^{\frac{2(2-\alpha)}{2\Delta_1}}, \quad (7)$$

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 [5]. The $\tau = (T/T_c) - 1$ 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

$$Y(q) = \left(\frac{q}{1+q} \right)^{2\Delta_1}, \quad (8)$$

where q is a renormalized distance to the critical point and can be found from the solution of the crossover sine-model (SM) [6] and

$$\left(q^2 - \frac{\tau}{Gi} \right) \left[1 - \frac{p^2}{4b^2} \left(1 - \frac{\tau}{q^2 Gi} \right) \right] = b^2 \left\{ \frac{\Delta\eta [1 + v_1 \exp(-10\Delta\eta)] + d_1 \tau}{m_0 Gi^{\beta}} \right\}^2 Y^{\frac{(1-2\beta)}{\Delta_1}}, \quad (9)$$

where b^2 is the universal linear-model parameter and p^2 the universal sine-model parameters, $p^2 = b^2 = 1.359$. The Gi is the Ginzburg number for the fluid of interest [7] and $m_0 = 1$ is set in this study and v_1 , d_1 , and Gi are the system-dependent parameters.

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

$$\bar{A}(T, v) = \Delta\bar{A}(\bar{\tau}, \bar{\varphi}) - \Delta v \bar{P}_0(T) + \bar{A}_0^r(T) + \bar{A}_0(T) - \ln v_{oc}, \quad (10)$$

where $\bar{A}_0^r(T)$ and $\bar{P}_0(T)$ are given by

$$\bar{A}_0^r(T) = r \left[-\frac{1}{\tilde{T}\tilde{v}_{oc}} + (\tilde{v}_{oc} - 1) \ln \left(1 - \frac{1}{\tilde{v}_{oc}} \right) + 1 \right], \quad (11)$$

$$\bar{P}_0(T) = r \left[-\tilde{v}_{oc} \ln \left(1 - \frac{1}{\tilde{v}_{oc}} \right) - \left(1 - \frac{1}{r} \right) - \frac{1}{\tilde{T}\tilde{v}_{oc}} \right]. \quad (12)$$

The critical part $\Delta\bar{A}$ is written as

$$\Delta\bar{A}(\bar{\tau}, \bar{\varphi}) = \bar{A}^r(\bar{\tau}, \bar{\varphi}) - \bar{A}^r(\bar{\tau}, 0) - \ln(\bar{\varphi} + 1) + \bar{\varphi} \bar{P}_0(\bar{\tau}, 0), \quad (13)$$

where $\bar{A}^r(\bar{\tau}, \bar{\varphi})$, $\bar{A}^r(\bar{\tau}, 0)$, and $\bar{P}_0(\bar{\tau}, 0)$ are given by

$$\bar{A}^r(\bar{\tau}, \bar{\varphi}) = r \left[-\frac{1}{\tilde{T}(1+\bar{\tau})\tilde{v}_{oc}(1+\bar{\varphi})} + (\tilde{v}_{oc}(1+\bar{\varphi}) - 1) \ln \left(1 - \frac{1}{\tilde{v}_{oc}(1+\bar{\varphi})} \right) + 1 \right], \quad (14)$$

$$\bar{A}^r(\bar{\tau}, 0) = r \left[-\frac{1}{\tilde{T}(1+\bar{\tau})\tilde{v}_{oc}} + (\tilde{v}_{oc} - 1) \ln \left(1 - \frac{1}{\tilde{v}_{oc}} \right) + 1 \right], \quad (15)$$

$$\bar{P}_0(\bar{\tau}, 0) = r \left[-\tilde{v}_{oc} \ln \left(1 - \frac{1}{\tilde{v}_{oc}} \right) - \left(1 - \frac{1}{r} \right) - \frac{1}{\tilde{T}(1+\bar{\tau})\tilde{v}_{oc}} \right]. \quad (16)$$

TABLE 1
System-dependent parameters for the xLF EOS

Components	Classical parameters			Crossover parameters		
	T^*/K	P^*/MPa	$\rho^*/(g \cdot cm^{-3})$	Gi	v_1	d_1
Carbon dioxide	266.25	617.82	1.345	0.0884	0.0034	3.232
Methane	205.35	234.15	0.449	0.0309	0.0032	3.084
Ethane	300.50	308.72	0.584	0.0884	0.0049	2.945
Propane	331.30	313.97	0.608	0.0490	0.0035	2.943
<i>n</i> -Butane	380.76	304.53	0.654	0.0425	0.0041	3.113
<i>i</i> -Butane	364.18	284.18	0.641	0.0441	0.0039	2.960
<i>n</i> -Pentane	415.67	285.77	0.664	0.0447	0.0038	2.639
<i>n</i> -Hexane	434.76	293.27	0.686	0.0296	0.0041	3.603
R123	404.30	337.85	1.661	0.0940	0.0049	2.989
R124	335.75	349.13	1.647	0.0890	0.0042	3.039
R125	286.05	368.27	1.730	0.0273	0.0042	4.207
R143a	291.90	389.03	1.254	0.1585	0.0026	4.219
R134a	313.17	403.06	1.450	0.0487	0.0249	3.040
R32	298.93	583.26	1.167	0.2093	0.0012	3.215
DME	350.62	433.98	0.760	0.0801	0.0029	3.041

Download English Version:

<https://daneshyari.com/en/article/217207>

Download Persian Version:

<https://daneshyari.com/article/217207>

[Daneshyari.com](https://daneshyari.com)