



Crossover parametric equation of state for asymmetric binary liquid system



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ARTICLE INFO

Article history:

Received 26 September 2013

Received in revised form 11 April 2014

Accepted 28 April 2014

Available online 10 May 2014

Keywords:

Parametric model

Complete scaling

Scaling field

Critical region

Refractive index

Thermodynamic properties

ABSTRACT

In the present work, using the principle of isomorphism and complete scaling method, a new scaled crossover parametric equation of state and a new representation for the refractive index of binary systems has been introduced. We have introduced a stepwise algorithm for calculating the mixing parameters defining scaling fields in terms of physical fields. Comparing the experimental data for five thermophysical properties and for eight binary liquid systems, it has been observed that this new approach is able to predict all thermophysical properties quite well.

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1. Introduction

Although mean-field theory is able to predict the thermophysical properties of fluids far from the critical point, this theory completely fails in the vicinity of the critical point and high deviations appear probably due to the long-range fluctuations in the order parameter. One possible approach to study the behavior of fluids and fluid mixtures close to the critical point is the renormalization group theory (RGT) [1]. RGT predicts that the free energy is a homogenous function of physical fields near the fixed points this result leads to the scaling law.

The scaling law is one of the most powerful tools to study the critical behavior of fluids and fluid mixtures in the vicinity of critical points and predicts that near the critical point, the thermophysical properties behave as [2,3]:

$$\Delta n_{\text{cxc}} = \hat{B}_0^n |\Delta \hat{T}|^\beta, \quad (1)$$

$$\Delta \hat{\rho}_{\text{cxc}} = \hat{B}_0 |\Delta \hat{T}|^\beta, \quad (2)$$

where n , $\hat{\rho}$ = $\frac{\rho}{\rho_c}$, $\Delta \hat{T} = \frac{T - T_c}{T_c}$ and β are the refractive index, reduced density, reduced difference temperature and universal critical exponent, respectively. Here, c and cxc stand for critical and coexistence, respectively. \hat{B}_0^n and \hat{B}_0 are two system dependent parameters.

Because of two important deficiencies of the lattice gas model, namely Yang–Yang anomaly and asymmetric nature of the coexistence curve, it was realized that this model is not able to give the correct prediction of the thermophysical properties of fluids in non-classical regions [4]. The lattice gas model does not cause Yang–Yang anomaly and predicts a perfect symmetry for the coexistence curves which is not correct for all fluids. One of the best ways for this problem was proposed by Fisher et al. [5], in which they suggested that the scaling fields should be a combination of all physical fields of the system. Using this assumption, called complete scaling, Kim et al. [6] showed that all physical behaviors of the system in the vicinity of critical point can be reproduced.

By using the principle of isomorphism implying that physical properties in coexisting phases can asymptotically exhibit universal power laws, thus we have added the difference of chemical potentials of the components to the scaling fields to extend the complete scaling to the binary systems [7,8].

Wang et al. [7] showed that the asymmetric nature of liquid–liquid coexistence was affected by the correlation between both concentration and entropy and concentration and density fluctuations.

Until now, no one has formulated a closed form representation for the scaling fields due to the mathematical problems appearing near the critical point. As a result, some parametric models have been proposed which can explain the behavior of the system close to the critical point where non-classical behaviors are enhanced [9].

Although this approach is very powerful to study the systems in the vicinity of the critical point, these kinds of equations of state have a very narrow range because the region in which fluids and fluid mixtures

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have long-range fluctuations is very small and exists close to the critical point. To extend the range of applicability of these equations of state, the crossover theory developed by the RGT of the critical phenomena is used. To this end, the scaling fields have been rescaled with respect to the fact that the crossover from asymptotic Ising-like critical behavior to classical mean-field behavior occurs by a crossover function [9].

Recently, Agayan et al. [9] have proposed a new crossover parametric model (CPM) which incorporates a crossover from non-classical to mean-field behavior. It was shown that CPM predicted thermophysical properties of ^3He accurately.

In this work, we have presented a new representation for refractive index using CPM and the resulting equation of state has been extended to binary systems in the complete scaling framework. Investigating the efficiency of the equation of state, we have adopted CPM for polar–nonpolar mixtures such as Benzonitrile + $n\text{-C}_n\text{H}_{2n+2}$ and Nitrobenzene + $n\text{-C}_n\text{H}_{2n+2}$ mixtures. Also, incorporating the CPM and complete scaling allows us to study the behavior of the fluid mixtures exhibiting asymmetric nature in their coexistence curves. It is worth noting that the above mentioned systems were selected because they have similar spatial structure solutions which lead to the same trends in the excess thermodynamic properties such as excess volume, excess isobaric heat capacity, and excess enthalpy, all with upper critical solution temperatures due to similar intermolecular interactions. These choices allow us to find out any trend in the system dependent coefficients.

This paper is organized as follows: in Section 2, we will review the scaling law, the complete scaling and the theory extended to the critical refractive index. In Section 3, the crossover parametric model will be discussed. Finally in Section 4, the CPM will be applied to the fluid mixtures and some physical systems will be considered showing the accuracy of the model.

2. Scaling law

It is well known that in the regions very close to the critical point, the critical behavior of fluids that belong to the universal class of Ising-like systems is characterized by two independent (h_1 and h_2) and one dependent (h_3) scaling fields. According to RGT, the relation between h_1 , h_2 and h_3 may be written as [10]:

$$h_3 \approx |h_2|^{2-\alpha} f^\pm \left(\frac{h_1}{h_2^{2-\alpha-\beta}} \right), \quad (3)$$

where α and β are universal exponents and superscripts + and – refer to $h_2 > 0$ and $h_2 < 0$, respectively. Using Eq. (3), one can calculate the scaling densities (φ_1 and φ_2) and susceptibilities (χ_1 and χ_2) [10] as follows:

$$\varphi_1 = \left(\frac{\partial h_3}{\partial h_1} \right)_{h_2} \approx \pm B_0 |h_2|^\beta, \quad h_2 \leq 0, \quad (4)$$

$$\varphi_2 = \left(\frac{\partial h_3}{\partial h_2} \right)_{h_1} = - \left(\frac{A_0^-}{1-\alpha} h_2 |h_2|^{-\alpha} - B_{cr} h_2 \right), \quad h_2 < 0 \quad (5)$$

$$\chi_1 = \left(\frac{\partial \varphi_1}{\partial h_1} \right)_{h_2} \approx \Gamma_0^\pm |h_2|^{-\gamma}, \quad (6)$$

$$\chi_2 = \left(\frac{\partial \varphi_2}{\partial h_2} \right)_{h_1} \approx A_0^- |h_2|^{-\alpha} - B_{cr}. \quad (7)$$

Thus, the two-phase isomorph heat capacity can be written as:

$$\hat{C}_{p,x}(x = x_c) = \left(\frac{\partial \varphi_2}{\partial h_2} \right)_{h_1} \approx \hat{A}_0^- |\Delta \hat{T}|^{-\alpha} - \hat{B}_{cr}, \quad (8)$$

where $\hat{C}_{p,x} = C_{p,x}/R$, and the heat capacity amplitudes are $\hat{B}_{cr} = B_{cr}/R$, $\hat{A}_0^- = A_0^-/\alpha R$.

In the lattice gas model the critical vapor–liquid transition can be identified by choosing the following fields [10]:

$$h_1 = \Delta \hat{\mu}, \quad h_2 = \Delta \hat{T}, \quad h_3 = \Delta \hat{P}, \quad (9)$$

where $\hat{T} = \frac{T}{T_c}$, $\hat{\mu} = \frac{\mu}{RT_c}$ and $\hat{P} = \frac{P}{R\rho_c T_c}$.

Although the Lattice gas model can predicts the non-classical behavior of the system close to the critical point, because of the perfect symmetry of its coexistence curve it is deeply understood that this model cannot be applied for real systems, as most of the fluids and fluid mixtures do not have perfect symmetry in their own coexistence curve [11,12].

Fisher et al. [5] proposed that the scaling fields should be a combination of all physical fields. Later, Wang et al. [4] using some assumptions have simplified the equations previously obtained by Fisher and co-workers and have shown that for scaling fields one can write:

$$\begin{aligned} h_1 &= a_1 \Delta \hat{\mu} + a_2 \Delta \hat{T} + a_3 \Delta \hat{P}, & h_2 &= b_1 \Delta \hat{T} + b_2 \Delta \hat{\mu} + b_3 \Delta \hat{P}, \\ h_3 &= c_1 \Delta \hat{P} + c_2 \Delta \hat{\mu} + c_3 \Delta \hat{T}, \end{aligned} \quad (10)$$

where coefficients a_i , b_i and c_i are system dependent parameters. As a consequence, thermophysical properties of the system can be obtained using Eqs. (4)–(5) and (10). For instance, density can be evaluated as [7]:

$$\hat{\rho} = \frac{1 + \varphi_1 + \varphi_2}{1 - a_3 \varphi_1 - b_3 \varphi_2}. \quad (11)$$

The complete scaling mentioned above cannot be used for a binary system. By using the principle of isomorphism, complete scaling can be extended to mixtures and to this end, the scaling fields are written as follows [7,13,14]:

$$h_1 = a_1 \Delta \hat{\mu}_1 + a_2 \Delta \hat{T} + a_3 \Delta \hat{P} + a_4 \Delta \hat{\mu}_{21} + a_5 \Delta \hat{E}', \quad (12)$$

$$h_2 = b_1 \Delta \hat{T} + b_2 \Delta \hat{\mu}_1 + b_3 \Delta \hat{P} + b_4 \Delta \hat{\mu}_{21} + b_5 \Delta \hat{E}', \quad (13)$$

$$h_3 = c_1 \Delta \hat{P} + c_2 \Delta \hat{\mu}_1 + c_3 \Delta \hat{T} + c_4 \Delta \hat{\mu}_{21} + c_5 \Delta \hat{E}', \quad (14)$$

where $\Delta \hat{\mu}_1$ is the chemical potential of component 1, $\Delta \hat{E}' \equiv E'/\rho_c k_B T_c$ is the reduced critical deviation of electric fields, recalling that $E' = \epsilon_0 E^2/2$ and $\Delta \hat{\mu}_{21}$ is the chemical potential difference of components 1 and 2.

The molecular density, $\hat{\rho}$, mole fraction, x_2 , entropy per unit volume, $\hat{\rho} \hat{S}$, molarity, $\hat{\rho} x_2$, (number of solute molecules per unit volume) and dielectric constant, ϵ_r , are defined as [13,14]:

$$\begin{aligned} \hat{\rho} &= \left(\frac{\partial \hat{P}}{\partial \hat{\mu}_1} \right)_{\hat{T}, \hat{\mu}_{21}, \hat{E}'}, & \hat{\rho} \hat{S} &= \left(\frac{\partial \hat{P}}{\partial \hat{T}} \right)_{\hat{\mu}_1, \hat{\mu}_{21}, \hat{E}'}, & \hat{\rho} x_2 &= \left(\frac{\partial \hat{P}}{\partial \hat{\mu}_{21}} \right)_{\hat{T}, \hat{\mu}_1, \hat{E}'}, \\ \epsilon_r &= \left(\frac{\partial \hat{P}}{\partial \hat{E}'} \right)_{\hat{T}, \hat{\mu}_1, \hat{\mu}_{21}}. \end{aligned} \quad (15)$$

Inserting Eq. (15) into Eqs. (12)–(14), thermodynamic relations of binary fluids may be written as [13,14]:

$$\begin{aligned} x_2 &= \frac{-c_4 + a_4 \varphi_1 + b_4 \varphi_2}{-c_2 + a_1 \varphi_1 + b_2 \varphi_2} = x_{2,c} + (1 - x_{2,c} a_1) \varphi_1 + (b_4 - x_{2,c} b_2) \varphi_2 \\ &\quad + (x_{2,c} a_1^2 - a_1) \varphi_1^2 + \dots, \end{aligned} \quad (16)$$

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