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Anomalous properties of dew-bubble curves in the vicinity of liquid–vapor critical points

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ABSTRACT

The explicit equation of dew-bubble curves in the vicinity of vapor–liquid critical points in mixtures has been derived within the scope of scaling theory and principle of isomorphism. It is shown that along these curves the pressure and the temperature depend non-analytically on the mixture density. As a consequence, the second derivatives $(d^2T/d\rho^2)_{\mathrm{DBC}}$ and $(d^2P/d\rho^2)_{\mathrm{DBC}}$ (taken along the dew-bubble curves) reveal cusp-like anomalies at the critical point. This specific feature enables one an easy estimation of the critical parameters of multicomponent mixtures directly from fitting a polynomial to dew-bubble-curve experimental data. To justify the proposed approach, the experimental data on dew-bubble curves for several binary and multicomponent mixtures have been analyzed and the positions of their critical points have been determined.

1. Introduction

One of the challenging problems arising from the study of phase behavior in multicomponent fluids is the reliable determination of their critical parameters. The knowledge of these parameters is necessary both for fundamental description of fluids and for various engineering applications. At present, there are several ways that are commonly used to determine the position of the vapor–liquid critical point. For example, the critical parameters can be calculated from empirical cubic equations of state (various modifications of the van der Waals equation) and from simulation studies of atomistic models. Such calculations need the exact knowledge of mixture composition and usually do not provide the required accuracy and reliability of the critical parameters.

Existing experimental techniques, in principle, can be used to directly determine the critical points of mixtures. The most direct experimental method is the measurement of the pressure dependence of liquid-phase amount at fixed temperature, i.e. the so-called isopletic line [1]. Unfortunately, this method has a serious drawback because of the need of visual observation of experimental sample. In addition, the amount of the liquid phase in the critical region changes abruptly, which may also decrease the accuracy in determination of the critical parameters.

Another way to obtain the critical parameters experimentally, in particular the critical density, is the analysis of discontinuities of the isochoric heat capacity $C_{\rho,x}$ and the temperature derivative of the pressure $(\partial P/\partial T)_{\rho,x}$ at the transition point between the two-phase and one-phase regions. Both jumps are known to be zero at a mixture critical point [2]. The study of the density dependencies of these jumps allows, in principle, to determine the isochore where the jumps are vanishing, thus the critical density can be established.

The measurement of anomalous behavior of physical characteristics of near-critical fluids ensures one more way to determine the mixture critical parameters. For example, measurements of $C_{\rho,x}$ and the derivative $(\partial P/\partial T)_{\rho,x}$ [2,3] as well as the measurements of the scattered-light intensity of the critical fluctuations [4–6] are suitable for this purpose. The drawback of such approach is that the observable anomalies of physical properties demonstrate relatively weak density dependence, so that it is hard to determine the critical isochore from the set of experimental data. To overcome such difficulty, one needs to possess very accurate experimental data obtained with small temperature and density steps. Description of thermodynamic properties of near-critical fluids based on the scaling theory also involves the location of mixture critical points [2]. The critical parameters are considered as adjustable ones and their values can be found from fitting the chosen theoretical model to the experimental data. However, the accuracy of the obtained critical-parameter values depends strongly on the

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chosen theoretical model as well as on the number of adjustable parameters. In addition, the need of the processing of a large number of experimental data with sophisticated software makes this approach time-consuming.

The present work suggests an alternative approach. Usually it is supposed that the location of the mixture critical point is not distinguished at the dew-bubble curve (DBC). However, in this work we show that the scaling theory and the principle of isomorphism, as specified in ref. [7], predict a specific cusp-like behavior in the vicinity of the liquid–vapor critical point for the second derivatives $(d^2T/d\rho^2)_{\mathrm{DBC}}$ and $(d^2P/d\rho^2)_{\mathrm{DBC}}$ taken along the dew-bubble curve. This fact provides the possibility to determine the critical parameters directly from analyses of DBC experimental data. The comparison of the results of this approach with the known values of the critical parameters of several previously studied mixtures demonstrates that the developed algorithm allows estimating the critical point position with sufficient accuracy.

2. Equation of state of a fluid mixture

A general approach to derive the equation of state of N-component mixture at fixed average composition x_i $(i=1,\ldots N)$ in the vicinity of its critical point has been developed in Ref. [7]. The approach is based on the critical-point universality and on the principle of isomorphism [8–10].

In the framework of this approach, physical properties of near-critical fluids are described in terms of ordering field h_1 and temperature-like field h_2. It is assumed that both fields are analytical functions of the reduced temperature τ and the chemical potentials of the mixture components $\Delta\mu_i$ and do not depend on the pressure. This is a simplification of the most general formulation of isomorphism given by the so-called complete scaling theory [11–16] where the physical properties of fluids are described in terms of the three scaling fields depending analytically not only on the reduced temperature τ and the chemical potentials of the mixture components $\Delta\mu_i$ but also on the pressure ΔP. As it is shown in Appendix, the results obtained for DBC in the framework of complete scaling are consistent with the results of our simplified approach.

The singular part of the thermodynamic potential near the critical point is the universal function of two scaling fields h_1 and h_2 [9,10] and the critical point corresponds to zero values of both fields, i.e. $h_1=h_2=0$. In main approximation the scaling fields can be written in the form

$$h_k=\sum_{i=1}^{N}a_{ki}\Delta\bar{\mu}_i+a_{k\tau}\tau+\ldots,\quad k=1,2. \tag{1}$$

Here $\tau=T/T_c-1$, $\Delta\bar{\mu}_i=\bar{\mu}_i-\bar{\mu}_{ic}$, where $\bar{\mu}_i=\mu_i/RT_c$ are the reduced chemical potentials conjugated to the partial molar density of a component, while T_c and $\bar{\mu}_{ic}$ are the critical values of the temperature and the chemical potentials of the components, and R is the universal gas constant. In fact, the Eq. (1) represents the well-known hypothesis of mixing of physical fields [17–19].

The density of the thermodynamic potential of a mixture for the given variables is the pressure P. Such potential is suitable since it depends on the thermodynamic variables which have the same values in coexisting phases. For the convenience we use the dimensionless pressure $\bar{P}=P/\rho_cRT_c$ where ρ_c is the molar critical density of the mixture. The differential of the pressure takes the form

$$d\bar{P}=\bar{s}d\tau+\sum_{i=1}^{N}\bar{\rho}x_i\,d\Delta\bar{\mu}_i, \tag{2}$$

where $\bar{s}=s/\rho_cR$ is the dimensionless entropy of the unit volume, x_i is the mole fraction of i-th component, and $\bar{\rho}=\rho/\rho_c$ is the reduced density of mixture. In the vicinity of the critical point of N-component mixture the pressure can be presented as a sum of singular P_s and regular P_r parts

$$\bar{P}(\tau,\Delta\bar{\mu}_i)=P_s(h_1,h_2)+P_r(\tau,\Delta\bar{\mu}_i), \tag{3}$$

where $i=1,\ldots,N$. The regular part of the pressure P_r is an analytical function of τ and $\Delta\bar{\mu}_i$. We would like to remark that in the framework of the complete scaling concept this division is automatically provided by mixing of all physical fields into the third scaling field. As it was mentioned above the singular part of the thermodynamic potential of a liquid mixture P_s can be parameterized in a universal way by means of two scaling fields, the ordering field h_1 and the thermal field h_2. Differential of P_s is defined as

$$dP_s=\varphi_2dh_2+\varphi_1dh_1. \tag{4}$$

Here the values φ_1 and φ_2 are scaling densities, the strongly fluctuating order parameter φ_1 and the weakly fluctuating density φ_2, conjugated to the scaling fields h_1 and h_2. The functional form of φ_1 and φ_2 coincide with the corresponding densities of 3D-Ising model [9].

The partial molar density of a component $\bar{\rho}x_i$ can be calculated as the first derivative of the pressure over the relevant chemical potential $\bar{\rho}x_i=(\partial\bar{P}/\partial\Delta\bar{\mu}_i)_{\tau,\Delta\bar{\mu}_{j\neq i}}$. Using Eq. (1) and expanding the regular part of the pressure in vicinity of the critical point over τ and $\Delta\bar{\mu}_i$, we obtain N equations of the form

$$\begin{aligned}\Delta\bar{\rho}\,x_i=(\bar{\rho}-1)x_i&=\sum_{k=1,2}\frac{\partial P_s}{\partial h_k}\frac{\partial h_k}{\partial\Delta\bar{\mu}_i}+\left(\frac{\partial P_r}{\partial\Delta\bar{\mu}_i}\right)_{\tau,\Delta\bar{\mu}_{j\neq i}}-x_i\\&=\varphi_1a_{1i}+\varphi_2a_{2i}+\sum_{j=1}^{N}b_{ij}\Delta\bar{\mu}_j+b_{i\tau}\tau+\cdots.\end{aligned} \tag{5}$$

The expansion coefficients $b_{i\tau}$ and b_{ij} are equal to the second derivatives of the P_r at the critical point, i.e. $b_{ij}=(\partial^2P_r/\partial\Delta\bar{\mu}_i\partial\Delta\bar{\mu}_j)^{(c)}$ and $b_{i\tau}=(\partial^2P_r/\partial\Delta\bar{\mu}_i\partial\tau)^{(c)}$. In one-phase region Eqs. (1) and (5) can be considered as $N+2$ equations for the unknown variables τ, $\Delta\bar{\rho}$ and $\Delta\bar{\mu}_i$. The solutions of this system can be presented as a series with respect to scaling densities φ_1,φ_2 and scaling fields h_1 and h_2 in the form

$$\Delta\bar{\mu}_i=c_{i1}\varphi_1+c_{i2}\varphi_2+c_{i3}h_2+c_{i4}h_1+c_{i5}\varphi_1^2+\ldots, \tag{6a}$$

$$\tau=c_{\tau1}\varphi_1+c_{\tau2}\varphi_2+c_{\tau3}h_2+c_{\tau4}h_1+c_{\tau5}\varphi_1^2+\ldots, \tag{6b}$$

$$\Delta\bar{\rho}=c_{\rho1}\varphi_1+c_{\rho2}\varphi_2+c_{\rho3}h_2+c_{\rho4}h_1+c_{\rho5}\varphi_1^2+\ldots. \tag{6c}$$

The substitution of the solutions for $\Delta\bar{\mu}_i$ and τ into the expansion of the regular part of the pressure P_r results in similar expression for the deviation of the pressure

$$\Delta\bar{P}=\bar{P}-\bar{P}_c=c_{p1}\varphi_1+c_{p2}\varphi_2+c_{p3}h_2+c_{p4}h_1+c_{p5}\varphi_1^2+\ldots. \tag{6d}$$

The scaling densities φ_1 and φ_2 in these equations are known universal functions of the scaling fields h_1 and h_2. The coefficients $c_{\tau i}$, $c_{\rho i}$, and c_{pi} depend on the concentrations in the fluid mixture. The terms proportional to φ_1^2 in Eqs. (6a)–(6d) and correspondingly, the terms proportional to $\Delta\rho^2$ in Eqs. (8a), (8b) (see below) arise due to the account of the second-order terms on $\Delta\mu_i$ and τ in Eqs. (1) and (5). The Eqs. (6a)–(6d) are valid both for pure fluids and for mixtures. For a one-component fluid the values τ and $\Delta\bar{\mu}_1$ can be expressed directly from Eqs. (1) as the expansions on h_1 and h_2 fields. It means that in pure fluids the coefficients $c_{11}=c_{12}=c_{15}=c_{\tau1}=c_{\tau2}=c_{\tau5}=0$. Correspondingly, the terms $\sim\varphi_1^2$ in coexistence curves of pure fluids may appear only due to the account of the ΔP terms in field mixing, i.e. in complete