



Simple approach to approximate predictions of the vapor–liquid equilibrium curve near the critical point and its application to Lennard-Jones fluids

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ABSTRACT

We propose a simple analytical form of the vapor–liquid equilibrium curve near the critical point for Lennard-Jones fluids. Coexistence densities curves and vapor pressure have been determined using the Van der Waals and Dieterici equation of state. In described method the Bernoulli differential equations, critical exponent theory and some type of Maxwell's criterion have been used. Presented approach has not yet been used to determine analytical form of phase curves as done in this Letter. Lennard-Jones fluids have been considered for analysis. Comparison with experimental data is done. The accuracy of the method is described.

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1. Introduction

An accurate knowledge of the equilibrium conditions is extremely important both in industry and science. Analytical form thermodynamic properties, like for example phase curves under equilibrium condition, are of special importance in physics, chemistry and engineering applications. Up to now several methods have been proposed to calculate vapor–liquid equilibrium (VLE) curves, one can distinguish among them theoretical, experimental and molecular simulation efforts, both for single and binary or ternary systems [1]. The most commonly used method is that one based on conventional Maxwell's procedure [2], which is based on the principle of equality of areas designated by the isotherm $T < T_c$ (if the saturated vapor is wavy) at the intersection of the isobars. In the two-phase region isobars should be chosen so that the field limited by the curve $T = const$ and the isobars is almost equal to zero. We know that the equation of state (EOS) also enables us to predict many useful thermodynamic properties, for example the equilibrium phase. Unfortunately, many forms of the used EOS only allow the approximate nature of the obtained results and the desired properties. The main reason is that every EOS operates only within the respective pressures or temperatures, moreover, constants appearing in every EOS are specific for each substances. Up to this day it is derived a universal EOS, successfully applied to any type of fluid which, applied to describe the

relationship between pressure, temperature and density, is true for all the real gases and plays the same role as the *Clapeyron* equation used in the ideal gases. This Letter presents a new mathematical approach to the problem of determining the coexistence curves of the VLE system.

We therefore pay attention to the method proposed by Okrański et al. [3]. In this method, they couple some type of Maxwell's construction with first-order nonlinear differential equations theory. However, they determined only numerical derivatives for the phase curves and at temperatures excluded near the critical point. In this Letter, we calculate the coexistence densities curves analytically, in very close vicinity of the critical point and propose useful, mathematically straightforward form of these phase curves, which can be successfully and easily used to calculate thermodynamic properties. As a basis of mathematical calculations there were used well-known and commonly used EOS for real gases – *Van der Waals (VdW)* and *Dieterici*. An analytical form of coexistence curve is an effect of correlating both, chosen EOS and method derived in [3], with the law of corresponding states, one of power laws for the VLE system and finally by solving two Bernoulli differential equations. As mentioned above we propose a simple analytical form of these curves and apply one of them (i.e. vapor density curve) for calculating the vapor pressure. In addition we apply this method to the Lennard-Jones (LJ) system and hence simple fluids such as liquid argon and liquid methane have been considered for analysis.

Besides a model presented by us has the following simplification and advantages over that proposed by Okrański et al. [3]: we do not use numerical methods to calculate the derivatives of

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the density liquid and vapor phase. We only use the value of the critical temperature of analyzed fluids, as the independent variable, which is the result of application of the law of corresponding states. We also eliminate adjustable parameters (constants contained in the used EOS), which are specific to each substance, by using the dimensionless variables (see also Section 2). We introduce the so-called deviation parameters to analyze the behavior of the system near the critical point and we propose an asymptotic form of EOS used to calculate the reduced parameters, and Taylor's theorem.

It should be noted that the model, proposed by us, is simple to use, permits one to calculate directly coexistence curves (from only a knowledge of the critical temperature of each substances) and is applicable only in immediate vicinity of the critical point of the VLE system. In addition it is in a good agreement with experimental data in the critical region, because usually the liquid phase densities are predicted to an accuracy of 1 to 2% in a wide temperature range, i.e. from triple point to the critical point. In contrast, our method gives comparable values (for both liquid and vapor phase) and works well near the critical region, where the thermodynamic parameters exhibit nonanalytical behavior which is very difficult to analyze.

We think, that the approach described in this work, may become an alternative method for testing the VLE systems, instead of so far used method based on Maxwell's rule.

2. Mathematical form of the coexistence densities curves versus critical exponent theory

Precise designation of the area in which the phases coexist with each other is not an easy task both from a mathematical and numerical point of view [4]. This poses many problems not only for physicists but also chemists and engineers who are trying to determine the properties of the equilibrium, back to the existing EOS or create new ones (based on experimental data or simulation [5]), for the analyzed problems.

Usually, to describe the equilibrium Maxwell's criterion is used [2]. Mathematical method described in this work is very general and is an analogue of Maxwell's method. It requires only knowledge of form of an analytical formula expressing the chemical potential $\mu = \mu(\rho, T)$ and the functional dependence $P = P(\rho, T)$ for the EOS (where the chemical potential, μ and the pressure, P are analytical functions of density, ρ and temperature, T) [4–6]. Determination of VLE properties is based on these two equations and the principle of equality of areas at a given temperature, which also corresponds to equality of chemical potentials in both phases. This equilibrium corresponds to the two curves: $\rho_L = \rho_L(T)$ and $\rho_V = \rho_V(T)$ defined in the area below the critical temperature.

It is known that for any temperature T below the critical T_c , the curves $\rho_L = \rho_L(T)$ and $\rho_V = \rho_V(T)$ satisfy the following system of equations:

$$P(\rho_V(T), T) = P(\rho_L(T), T), \quad \mu(\rho_V(T), T) = \mu(\rho_L(T), T) \quad (1)$$

Differentiating Eqs. (1) with respect to T [3], we can obtain the differential form of the curves $\dot{\rho}_L = f(\rho_L, \rho_V, T)$ and $\dot{\rho}_V = f(\rho_V, \rho_L, T)$ in the near-critical region (denote the first-order derivatives of $\rho_L(T)$ and $\rho_V(T)$ with respect to T), where function f is of the form

$$f(\rho_V, \rho_L, T) = \frac{\left(\frac{\partial \mu}{\partial T}(\rho_V, T) - \frac{\partial \mu}{\partial T}(\rho_L, T)\right) \rho_V \rho_L + \left(\frac{\partial P}{\partial T}(\rho_L, T) - \frac{\partial P}{\partial T}(\rho_V, T)\right) \rho_V}{\frac{\partial P}{\partial \rho}(\rho_V, T)(\rho_V - \rho_L)} \quad (1a)$$

The right side of Eq. (1a) is regular and hence we can find a unique solution in the form of curves ρ_L and ρ_V for given initial conditions $\rho_V^0 = \rho_V(T_0)$, $\rho_L^0 = \rho_L(T_0)$ and temperature $T_0 < T_c$. Furthermore, we assume that $\rho_V(T) < \rho_L(T)$ for $T < T_c$ and the critical point $\rho_V(T_c) = \rho_L(T_c) = \rho_c$ (where (ρ_c, T_c) determines the so-called critical point and ρ_c and T_c denote the density and critical temperature, respectively).

In this place we must mention that the expressions (1) and (1a) allow strictly determination of phase curves in area of their coexistence, but the use of many simplifications in the calculation (see the Introduction and Section 2.1) leads to only obtaining an approximate formula of coexistence densities curves near the critical point, with deviations not less than 1.5%, for the test substances.

Usually it is almost impossible to appoint a strict, analytical solution of differential form of curves given by formula (1a), for given P and μ , and numerical method must be used [7–11]. We modified method proposed in [3] correlating it with the quantitative description of the phenomena associated with the phase transitions. Below a simple mathematical way to obtain these curves (expressed in analytical form) is presented.

2.1. Van der Waals equation – critical exponent theory and coexistence densities curves

Consider the popular and often used VdW EOS [12] for real gases in the form

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \quad (2)$$

where P – pressure, V – volume, R – universal gas constant, a represents attraction arising from dispersion forces, b accounts for the volume occupied by the molecules.

Substituting the relation $\rho = m/V = 1/V$ we obtain

$$P = \frac{RT\rho}{1-\rho b} - a\rho^2 \quad (3)$$

At critical temperature, we know that

$$\left(\frac{\partial P}{\partial \rho}\right)_{T_c} = \left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T_c} = 0 \quad (4)$$

hence we determine the critical parameters

$$\rho_c = \frac{1}{3b}, \quad P_c = \frac{a}{27b^2} = \frac{RT_c}{8b}, \quad T_c = \frac{8a}{27bR} \quad (4a)$$

Using the dimensionless variables

$$T_r = \frac{T}{T_c}, \quad P_r = \frac{P}{P_c}, \quad \rho_r = \frac{\rho}{\rho_c} \quad (5)$$

determines the so-called reduced VdW EOS (without constants which are specific for each substances)

$$P_r = \frac{8T_r\rho_r}{3-\rho_r} - 3\rho_r^2 \quad (6)$$

Using the reduced parameters allows meaningful analysis of the behavior of the investigated system, not only in the two-phase region, but also in the near-critical region. As seen above (4a), the reducing parameters are experimentally measured coordinates of the critical point (temperature, pressure and density respectively). The correct description of the system near a critical point offers the so-called deviation parameters

$$p = P_r - 1, \quad t = T_r - 1, \quad \tilde{\rho} = \rho_r - 1 \quad (7)$$

Substituting (7) into (3) we obtain

$$p = \frac{8(t+1)(\tilde{\rho}+1)}{(2-\tilde{\rho})} - 3(\tilde{\rho}+1)^2 - 1 \quad (8)$$

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