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ORIGINAL PAPER

On approximate mathematical modeling of the vapor–liquid coexistence curves by the Van der Waals equation of state and non-classical value of the critical exponent

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Abstract Van der Waals equation of state as well as power laws and critical exponent theories are prototypes to study the cubic shape, asymmetries and "flatness" of the vapor–liquid equilibrium curves near the critical point. In this work we study two similar methods to determine the phase curves in analytical form, which differ from each other by simplicity of mathematical calculation. We analyze temperature dependence of the coexistence curves asymptotically close to the vapor–liquid critical point. We explain the novelty of our method with respect to the standard thermodynamic limit discussed in the literature. Therefore we show that the shape of the coexistence curves can strongly influence the accepted value of the critical exponent. The results of theoretical studies have been compared with the ones obtained by experimental methods.

Keywords Vapor–liquid critical point · Order parameter · Power laws · Integral equations · Power series

1 Introduction

An analysis and precise knowledge of the critical region of different substances is very important issue, from both theoretical and practical point of view. For this reason prediction of the thermodynamics potential it is essential to use reliable model that, if possible, generates quite accurate results using simple procedure. This fact leads

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us to search for mathematically simply way, enabling the simplest description of this complex area, in which it is desired the ability to predict anomalous behavior of thermodynamic properties.

Critical area and hence the phenomenon occurring in it are extensively discussed subject of scientific studies, which often refer to advanced methods of functional analysis, quantum mechanics [1–4] or to use only approximate numerical method for the presented problems [5–12]. On purpose of our research is primarily to demonstrate that the description of the critical region can be done, from a mathematical point of view, in a very simple way, using the known laws of physics and performing intermediate mathematical calculations. This paper presents new mathematical approach to the problem of describing the asymptotic vicinity of the vapor–liquid equilibrium (VLE) system near the vapor–liquid critical point by determining the vapor–liquid coexistence curves.

In the general case the key problem which appears in thermodynamic description of the critical region is based on fact that the thermodynamic model must be quite accurate when compared with experimental data. In addition it should be mathematically straightforward, so as to be easy to handle in the calculation of thermodynamic parameters.

Presented below the results of the analytical calculations, and thus the same mathematical description of the vapor–liquid critical region has been imported to solve system of nonlinear Bernoulli differential equations. These equations were derived directly from the asymptotic form of the Van der Waals equation of state (VdW EOS) for real gases by using Taylor's theorem and deviation parameters [see Eq. (1)] [13].

System of nonlinear differential equations were solved in connection with the classical Maxwell's rule and integral equations, thus putting the compatibility of mathematical description with the physical fundamentals of the analyzed phenomenon.

In turn, integrating the methods of power series with the previously mentioned the Maxwell's rule and the classical Van der Waals suggestion, allowed us to correct fractional exponents for one of the thermodynamic potentials. As a result, we obtained to solve simple third degree polynomial directly from the Cardano formulas and in consequence we derived a simple analytical form of coexistence curves in cubic shape.

The approach presented in [13] has been refined by: illustrating usefulness of the asymptotic form of the VdW EOS, which we use it to calculation, both with the value of critical exponent close this observed experimentally. We develop a new analytical form of coexistence curves in cubic shape in asymptotic vicinity of the vapor–liquid critical point. Two equivalent (from mathematical and physical point of view) means to determine these curves have been presented. Next we have tried to prove that under certain assumptions, can be almost directly use the VdW theory and VdW EOS, both confirm and obtain, on the basis of simple mathematical calculations, phase curves in cubic shape. Cubic shape of the phase curves consistent with experimental results. This fact to this day leads to conflict between the classical theory and experiment. What's more we derived, probably the first, a simple analytical form of cubic shape of these curves (based on the asymptotic form of the VdW EOS) and we testified their quite good accuracy by comparison with real data. Furthermore, as shown in Sect. 2, the calculations were carried out separately for each phase, which in turn verified the asymmetry of the coexistence curves, not only from the analytical results, but also by numerical estimation of the real data [14–17] (compare also Sect. 3.1). In the end unlike other models, asymptotic form of the VdW EOS is capable of predicting the flatness of the coexistence curves [18], which often occurs in real fluids of the Lennard-Jones type [13] (see Sect. 3.1).

Nonanalicity of the thermodynamic potentials used for the calculations have been avoided by introducing so-called deviation parameters ('distance' from the critical point) for each of them, such as pressure, temperature and density [13] (where P is the pressure and P_c is the critical pressure of the liquid).

$$p = \frac{P}{P_c} - 1, \quad t = \frac{T}{T_c} - 1, \quad \tilde{\rho} = \frac{\rho}{\rho_c} - 1 \tag{1}$$

This procedure resulted the possibility of applying of transformations and mathematical methods and allows us to analytic form used for the calculation of EOS at the critical point and its immediate vicinity, leading to the analytical form of the coexistence curves in cubic shape.

As mentioned above in the asymptotic vicinity of the critical point occurs the problem determining the functional relationships between the thermodynamic potentials, which exhibit nonanalytical behavior at this point. The reason of these behaviors affect the difficulty of the experimental analysis of the thermodynamic properties. And hence we correlate approximate description of the critical area of the VLE system with power laws, critical exponents theory and differential equations theory. This has its strict justification because it is commonly known that the liquid state is characterized by anomalous fluctuations of the order parameter near the critical point [19,20]. Some kind of singularity of the thermodynamic potentials at this point is the immediate cause of these fluctuations [21].

To this day several methods have been proposed for the quantitative and semi quantitative analysis of the behavior of the various pure fluids near the critical point. Some of them use non-classical value of the critical exponent (close to those observed experimentally) [22], for example the method based on the phase-space cells approximation introduced by Wilson [1,2], Wilson and Fisher [23], Grover [24], Grover et al. [25], Salvino and White [26].

In this paper we also extend the Van der Waals [27] suggestion that the coexistence curve is parabolic in shape and as Levelt Sengers et al. [28] we pointed out that the shape of the coexistence curve near the critical point is more cubic than parabolic, for a single component. This fact leads to conflict between the classical theory (see Table 1) and experiment because in general case the VdW EOS accounts qualitatively for VLE and the existence of the critical point.

Up to now the question of the shape of the coexistence curve near the critical point has been much discussed [29–34]. To underline the importance of the coexistence curve cubic shape Guggenheim [29], Croxton [30], Wyczałkowska et al. [31], Weinberger and Schneider [32], Widom and Rice [33], Zimm [34] proposed a correlation between the order parameter of liquid–vapor system with temperature (where ρ_L, ρ_V, T, T_c are the density of the liquid and vapor phase, temperature and critical temperature of the liquid, respectively), by the equation

Table 1 Select the power laws, values of critical index and the ways of achieving the critical point for liquid-saturated vapor system (when $t = \frac{T}{T_c} - 1$) [36]

Critical index	Power laws	Trajectory	Experimental results	Mean field approaches
α	$C_v \sim (\pm t)^{-\alpha}$	Critical isochore	0.110 ± 0.003	0
β	$\rho_L - \rho_V \sim (-t)^{-\beta}$	Coexistence curve	0.326 ± 0.002	0.5
γ	$\kappa_T \sim (\pm t)^{-\gamma}$	Critical isochore	1.239 ± 0.002	1

$$\rho_L - \rho_V = k\,(T_c - T)^{1/3} \tag{2}$$

In our work, as a basic of mathematical calculations there were used asymptotic form of the VdW EOS and the value of the order parameter, which derives directly from the power laws where the critical point is achieved asymptotically along the coexistence curve (see Table 1), i.e. depending [where $\boldsymbol{t}$ is given by (1)]

$$\rho_L - \rho_V = (-t)^{-\beta} \tag{3}$$

The exception was the only accepted value of the critical exponent, which is not selected on the basis of predictions of classical theory but the experiment (see Table 1) and observation contained in the work of Levelt Sengers [28]. We noting that the value of the critical exponent β ≈ 0.326 ≈ 0.33 ≈ 1/3 and agrees with the value adopted by Guggenheim [29–34].

2 Mathematical and physical derivation of the method: the critical region of the VLE system

It is known that important aspect of the critical region is that most of the anomalies in the thermodynamic properties can be set in the form of universal power laws with respect to the critical-point parameters. Critical point of the vapor–liquid system is the reference point, from which all of the transition properties of such a fluid can be derived. In addition this is the point, characterized by a fixed temperature, pressure and density, at which the distinction between the gas and the liquid phase simply disappears. From both scientific and technological point of view the transition between the vapor and liquid phases of a pure fluids is one of fundamental in nature.

Around the critical point parameter such as the density of the liquid and vapor phases obeys universal power laws. This parameter we can easily vary by using, for example, small changes of temperature (see also Table 1). Because the liquid and vapor phases coexist with different densities, density of the fluid is inhomogeneous below the critical point.

Very useful and mathematically straightforward method to determine the VLE curves in parabolic shape, in the case when the critical point is achieved asymptotically along the coexistence curve in [13] has been proposed. As a first approximation we consider well-known and commonly used VdW EOS in the form (after using the substitution $\rho = m/V = 1/V$ in the place of volume V):

$$P = \frac{RT\rho}{1-\rho b} - a\rho^2 \tag{4}$$

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

Next we leading this equation to the simple asymptotic form (see Eq. 4a) by meeting several general requirements, generally by used to calculate the deviation parameters (1) and Taylor's theorem:

$$p\left(\tilde{\rho}, t\right) = t\left(4 + 6\tilde{\rho}\right) + 3\tilde{\rho}^3 \tag{4a}$$

Thermodynamic properties of the VLE system and the same the curves $\rho_L = \rho_L(T)$, $\rho_V = \rho_V(T)$, for any temperature $T < T_c$ can be easily find from the following system of equations

$$P(\rho_V(T),\ T) = P(\rho_L(T), T), \quad \mu(\rho_V(T),\ T) = \mu(\rho_L(T), T) \tag{5}$$

The condition (5) 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.

We can simply obtain differential form of the coexistence curves near critical region directly from the system of equations [where $\dot{\rho}_L$ and $\dot{\rho}_V$ denote the first-order derivatives of $\rho_L(T)$ and $\rho_V(T)$ with respect to T, see also Eq. (5)]:

$$\dot{\rho}_L = f(\rho_L, \rho_V, T) \quad \dot{\rho}_V = f(\rho_V, \rho_L, T) \tag{6}$$

where function f is of the form

$$f\left(\rho_V, \rho_L, T\right) = \frac{\left(\frac{\partial\mu}{\partial T}\left(\rho_V, T\right) - \frac{\partial\mu}{\partial T}\left(\rho_L, T\right)\right)\rho_V\rho_L + \left(\frac{\partial P}{\partial T}\left(\rho_L, T\right) - \frac{\partial P}{\partial T}\left(\rho_V, T\right)\right)\rho_V}{\frac{\partial P}{\partial \rho}\left(\rho_V, T\right)\left(\rho_V - \rho_L\right)} \tag{6a}$$

This formula is the effect differentiating Eq. (5) with respect to T [35] (where the chemical potential, μ and the pressure, P are analytical functions of density, ρ and temperature, T)

Because the right side of the Eq. (6a) is regular, we can find an unique solution in the form of curves ρ_L and ρ_V for given initial conditions $\rho_V^0 = \rho_V\left(T_0\right)$, $\rho_L^0 = \rho_L\left(T_0\right)$ and temperature $T_0 < T_c$. In addition assuming that $\rho_V(T) < \rho_L(T)$ for $T < T_c$, the critical point of density can be obtain by $\rho_V(T_c) = \rho_L(T_c) = \rho_c$ (where (ρ_c, T_c) determines the so-called critical point and ρ_c, T_c denote, as above, the critical density and critical temperature). We must note, that the expressions (6) and (6a) allow for strictly determination of phase curves in area of their coexistence, but the use of many simplifications in the calculation [13] leads to obtaining only an approximate formula of phase curves in cubic shape, near the vapor–liquid critical point.

As it turns out the determined phase curves can be successfully used to calculate one of thermodynamics potential and describes, in semi quantitative way, the asymptotic vicinity of the vapor –liquid critical point.

2.1 Analytical consideration of the method: asymptotic form of the Van der Waals EOS

Derived in [13] nonlinear differential form of the coexistence densities curves for the VdW EOS are given by expressions below

$$\dot{\tilde{\rho}}_V = \frac{(\tilde{\rho}_L - \tilde{\rho}_V)}{\left(2t - 4\tilde{\rho}_V + \frac{3}{2}\tilde{\rho}_V^2\right)}, \quad \dot{\tilde{\rho}}_L = \frac{(\tilde{\rho}_V - \tilde{\rho}_L)}{\left(2t - 4\tilde{\rho}_L + \frac{3}{2}\tilde{\rho}_L^2\right)} \tag{7}$$

Using the substitution $\tilde{\rho}_L - \tilde{\rho}_V = (-t)^{-1/3}$ [see also Eq. (2)] we can import a nonlinear differential equations (7) to linear form

$$\dot{\tilde{\rho}}_V(t) = \frac{1}{\sqrt[3]{-t}\left(2t - 4\tilde{\rho}_V + \frac{3}{2}\tilde{\rho}_V^2\right)} \quad \dot{\tilde{\rho}}_L(t) = \frac{-1}{\sqrt[3]{-t}\left(2t - 4\tilde{\rho}_L + \frac{3}{2}\tilde{\rho}_L^2\right)} \tag{8}$$

At the beginning let us consider the differential equation for the saturated vapor density. The Eq. (8) may be written as (at the assumption that $\boldsymbol{\tilde{\rho}_V} \neq 0$)

$$\frac{d\tilde{\rho}_V}{dt} = \frac{1}{\sqrt[3]{-t}\left(2t - 4\tilde{\rho}_V + \frac{3}{2}\tilde{\rho}_V^2\right)} \tag{9}$$

what leads to obtaining a simple, *Bernoulli* differential equation with parameter $n = 1/3$,

$$\frac{dt}{d\tilde{\rho}_V} - (-t)^{1/3}\left(\frac{3}{2}\tilde{\rho}_V^2 - 4\tilde{\rho}_V\right) - 2(-t)^{4/3} = 0 \tag{10}$$

Dividing (10) by $(-t)^{1/3}$ we get

$$\frac{t'}{(-t)^{1/3}} - \left(\frac{3}{2}\tilde{\rho}_V^2 - 4\tilde{\rho}_V\right) - 2(-t) = 0 \tag{11}$$

Now we use the substitution $z = (-t)^{1-n}$, where $n = 1/3$, from this we have

$$z' - \frac{4}{3}z^{3/2} = -\tilde{\rho}_V^2 + \frac{8}{3}\tilde{\rho}_V \tag{12}$$

The question about solve of this equation is answered by use the following, conventional Maxwell's procedure [36]. It is well-known that the form of the coexistence curve can be determined, equivalently, from the equality of the chemical potentials for the coexisting phases, or from Maxwell's rule. Hence for the two-phase region

$(\tilde{\rho}_V, \tilde{\rho}_L)$ we can transform (12) into an equivalent integral equation, knowing that in our model the value of the saturated vapor density in the coexistence region is negative, given by

$$z(0) - z(-x) = -\frac{1}{3}x^3 - \frac{4}{3}x^2 + \frac{4}{3}\int\limits_{-x}^{0} z^{3/2}(x)dx \tag{13}$$

where we denoted (for clarity) $x = \tilde{\rho}_V(t)$, $z(0) = 0$, $z(x) = (-t)^{2/3}$. From property of even function $z(x)$ we have that $z(-x) = z(x)$. To obtain a simpler form (no fractional values generated after integration $\int_{-x}^{0} z^{3/2}(x)dx$ relative to the saturated vapor density) solution of Eq. (13) we make a simplification, assuming that the value of integrate $4/3\int_{-x}^{0} z^{3/2}(x)\,dx$ is sufficiently small and is equal to zero (because in two-phase region in this case we have a situation when the density of the vapor phase asymptotically goes to the critical point, and hence for $x \to 0$ we have also $z(x) \to 0$, where the point $(t, \tilde{\rho}) = (0, 0)$ is set as the critical point). In this case the solution of Eq. (13) is given by a third degree polynomial

$$x^3 + 4x^2 - 3(-t)^{2/3} = 0 \tag{14}$$

Solving this equation we use the *Cardano* formulas that eventually will get the approximate curve corresponding to the density of the saturated vapor phase in the analyzed area. Substitution in this equation $x = w - 4/3$ gives

$$w^3 - \frac{16}{3}w - \frac{128}{27} - 3(-t)^{2/3} = 0 \tag{15}$$

Setting the delta for this equation

$$\Delta = \frac{9}{4}(-t)^{4/3} + \frac{64}{9}(-t)^{2/3} \tag{16}$$

we can finally determine the approximate coexistence curve for the vapor phase, near the critical point, described by the equation

$$\tilde{\rho}_V(t) = \sqrt[3]{\frac{64}{27} + \frac{3}{2}(-t)^{2/3} - \sqrt{\Delta}} + \sqrt[3]{\frac{64}{27} + \frac{3}{2}(-t)^{2/3} + \sqrt{\Delta}} - \frac{4}{3}, \tag{17}$$

Similar procedure we apply to the liquid phase, and in this case, after assumption that $\boldsymbol{\tilde{\rho}_L} \neq 0$, the Bernoulli differential equation with parameter $n = 1/3$ is in the form

$$\frac{dt}{d\tilde{\rho}_L} + (-t)^{1/3}\left(\frac{3}{2}\tilde{\rho}_L^2 - 4\tilde{\rho}_L\right) + 2(-t)^{4/3} = 0 \tag{18}$$

In this case, after dividing (18) by $(-t)^{1/3}$ and using the substitution $z = (-t)^{1-n}$ for $n = 1/3$, we have

$$z' - \frac{4}{3}z^{3/2} = \tilde{\rho}_L^2 - \frac{8}{3}\tilde{\rho}_L \tag{19}$$

As mentioned above, from the conventional Maxwell's procedure, for the two-phase region $(\tilde{\rho}_V, \tilde{\rho}_L)$, we can transform (19) into equivalent integral equation, knowing that the value of the liquid density in the coexistence region is positive, given by

$$z(y) - z(0) = \frac{1}{3}y^3 - \frac{4}{3}y^2 - \frac{4}{3}\int\limits_0^y z^{3/2}(y)dy \tag{20}$$

where we denoted (for clarity) $y = \tilde{\rho}_L(t)$, $z(y) = (-t)^{2/3}$, $z(0) = 0$. Then (from the same reasons as above) we assume that the value of integrate $4/3\int_0^y z^{3/2}(y)dy$ is sufficiently small and is equal to zero (because in two-phase region in this case we have a situation when the density of the liquid phase asymptotically goes to the critical point, and hence for $y \to 0$ we have also $z(y) \to 0$).

The same procedure applied now to the liquid phase, as above to the vapor phase, gives us the final solution in the form

$$\tilde{\rho}_L(t) = \sqrt[3]{\frac{64}{27} + \frac{3}{2}(-t)^{2/3} - \sqrt{\Delta}} + \sqrt[3]{\frac{64}{27} + \frac{3}{2}(-t)^{2/3} + \sqrt{\Delta}} + \frac{4}{3} \tag{21}$$

where the delta is also given by (16).

Now consider the case when the values of integrals in Eqs. (13) and (20) are not equal to zero. Taking into account, in this place, the Van der Waals suggestion [27] that the coexistence curve is parabolic in shape in the region of coexistence of phases for the temperature–density plane, we can use the following corrections for the vapor phase describing by Eq. (13)

$$\frac{4}{3}\int\limits_{-x}^{0} z^{3/2}(x)dx \approx \frac{4}{3}\int\limits_{-x}^{0} z^2(x)dx \tag{22}$$

where $z^2(x)$ is the reduced temperature along the isochore $\rho = \tilde{\rho}_V$ and the integral is taken along the vapor phase, which is negative in this region (because to our assumption $\rho_V(t) < \rho_L(t)$ for $T < T_c$ we have also $\tilde{\rho}_V(t) < 0$ and $\tilde{\rho}_L(t) > 0$). Acting in this way we can eliminate the fractional index appearing in Eq. (13).

We deduce from (22) that Eq. (13) corresponds to the form

$$-(t)^{2/3} = -\frac{1}{3}x^3 - \frac{4}{3}x^2 + \frac{4}{3}\int\limits_{-x}^{0} z^2(x)dx$$

after integration we have

$$-\left(t\right)^{2/3}=-\frac{1}{3}x^{3}-\frac{4}{3}x^{2}+\frac{4}{9}x^{3}\rightarrow-\left(t\right)^{2/3}=\frac{1}{9}x^{3}-\frac{4}{3}x^{2}$$

And as mentioned above the solution of this equation is given by a third degree polynomial

$$x^{3}-12x^{2}+9\left(-t\right)^{2/3}=0 \tag{23}$$

Finally it is easy to calculate that

$$\tilde{\rho}_{V}\left(t\right)=\sqrt[3]{\frac{9}{2}\left(-t\right)^{2/3}-64-\sqrt{\Delta}}+\sqrt[3]{\frac{9}{2}\left(-t\right)^{2/3}-64+\sqrt{\Delta}}+4 \tag{24}$$

where $\Delta=8192+\frac{81}{4}\left(-t\right)^{4/3}-576\left(-t\right)^{2/3}$

From the same reason for the liquid phase we have the final solution given by (when we use for calculation condition given by formula (22), where $z^{2}(y)$ is, in this case, the reduced temperature along the isochore $\rho=\tilde{\rho}_{L}$ and the integral is taken along the liquid phase, which is positive in this region)

$$\tilde{\rho}_{L}\left(t\right)=\sqrt[3]{\frac{64}{343}+\frac{9}{14}\left(-t\right)^{2/3}-\sqrt{\Delta}}+\sqrt[3]{\frac{64}{343}+\frac{9}{14}\left(-t\right)^{2/3}+\sqrt{\Delta}}+\frac{4}{7} \tag{25}$$

for $\Delta=\frac{81}{196}\left(-t\right)^{4/3}+\frac{576}{2401}\left(-t\right)^{2/3}$

Taking into account the assumption $\tilde{\rho}_{V}(t)<\tilde{\rho}_{L}(t)$ for $T<T_{c}$, the approximate coexistence curve in asymptotic vicinity of the critical point is described by the equations:

(17)—for the vapor phase, (21)—for the liquid phase (without correction)
(24)—for the vapor phase, (25)—for the liquid phase (with correction).

2.2 Analytical consideration of the method: alternative approach to determine the phase curves from the asymptotic form of the VdW EOS

In this section we show another mathematical way to solve Bernoulli differential equations [see Eqs. (12), (19)], from which almost immediately, we can determine simple analytical form for the phase curves in cubic shape. In this case to solve the Bernoulli differential equations (12), (19) we use so-called power series method. At the beginning we rewrite Eq. (12)

$$z'-\frac{4}{3}z^{3/2}=-\tilde{\rho}_{V}^{2}+\frac{8}{3}\tilde{\rho}_{V}$$

Now to avoid the fractional index occurring in this equation (because we want to apply the power series method), we use the same as above, mathematical substitution, based on the Van der Waals suggestion that the coexistence curve is parabolic in shape in the region of coexistence of phases for the temperature–density plane. Hence we can use the following corrections for the vapor phase described by (12) i.e.

$$\frac{4}{3}z^{3/2} \approx \frac{4}{3}z^{2}$$

Then the expression (12) simplifies to the form

$$z' - \frac{4}{3}z^{2} = -\tilde{\rho}_V^{2} + \frac{8}{3}\tilde{\rho}_V \tag{26}$$

And in consequence we can assume that the solutions of the Eq. (26) are given by the form

$$z\left(x\right) = \sum_{n=0}^{\infty} a_n x^n$$

where we use the same notation as above i.e. $x = \tilde{\rho}_V\left(t\right),\ z\left(x\right) = \left(-t\right)^{2/3}$. Then we have also

$$z'\left(x\right) = \sum_{n=1}^{\infty} n a_n x^{n-1}$$

and the left side of Eq. (26) reduces to the simple form of the power series, with the initial condition $z(0) = 0$

$$\sum_{n=1}^{\infty} n a_n x^{n-1} - \frac{4}{3}\left(\sum_{n=0}^{\infty} a_n x^n\right)^2 = -x^2 + \frac{8}{3}x \tag{26a}$$

Let us note that the right side of Eq. (26a) is already in a power series expand some of parabolic function. Solving it we find the constants a_n given by $a_0 = a_1 = 0$, $a_2 = 3/16,\ a_3 = -1/3,\ a_{n+1} = 0$, for $n \geq 3$. Finally the approximate solution (26a) leads to the third degree polynomial given by expression

$$x^3 - \frac{9}{16}x^2 + 3\left(-t\right)^{2/3} = 0 \tag{27}$$

We solve it and find that the approximate coexistence curve, near the critical point, is described by the equation

$$\tilde{\rho}_V\left(t\right) = \sqrt[3]{-\frac{3}{2}\left(-t\right)^{2/3} + \frac{27}{4096} - \sqrt{\Delta}} + \sqrt[3]{-\frac{3}{2}\left(-t\right)^{2/3} + \frac{27}{4096} + \sqrt{\Delta}} + \frac{3}{16} \tag{28}$$

for $\Delta = \frac{193}{8388608} + \frac{9}{4}\left(-t\right)^{4/3} - \frac{81}{4096}\left(-t\right)^{2/3}$.

Analogous procedure used in relation to the liquid phase described by (19), in this case, assuming $y = \tilde{\rho}_L(t)$, $z(y) = (-t)^{2/3}$, with the initial condition $z(0) = 0$, also leads to obtain the relation

$$\sum_{n=1}^{\infty} n a_n y^{n-1} - \frac{4}{3}\left(\sum_{n=0}^{\infty} a_n y^n\right)^2 = y^2 - \frac{8}{3}y \tag{29}$$

with the constants, after calculating it, $a_0 = a_1 = 0, a_2 = -3/16, a_3 = 1/3, a_{n+1} = 0$, for $n \geq 3$. The approximate solution is, similarly as it was in the case for the saturated vapor phase, given by the third degree polynomial

$$y^3 - \frac{9}{16}y^2 - 3(-t)^{2/3} = 0 \tag{30}$$

Solving it we have

$$\tilde{\rho}_L(t) = \sqrt[3]{\frac{3}{2}(-t)^{2/3} + \frac{27}{4096} - \sqrt{\Delta}} + \sqrt[3]{\frac{3}{2}(-t)^{2/3} + \frac{27}{4096} + \sqrt{\Delta}} + \frac{3}{16} \tag{31}$$

with $\Delta = \frac{193}{8388608} + \frac{9}{4}(-t)^{4/3} + \frac{81}{4096}(-t)^{2/3}$.

In the end we have second alternative solutions of Eqs. (12), (19) in cubic function form, described by (28)—for the vapor phase, and (31)—for the liquid phase.

3 Results and discussion

In this section we present the results of fitting our method to the experimental data. We present determined in Sects. 2.1 and 2.2 phase curves in temperature–density plane. In simulation as input only the value of the critical temperature fluids analyzed is needed, as the independent variable, because it is the result of application in calculation the law of corresponding states (for more details see also [13]).

To test the validity of Eqs. (24), (25), (28), (31) for pρt data in the close vicinity of the critical point, we used experimental data for fluids of different kinds, such as diatomic and polyatomic molecules i.e. hydrogen (H_2), oxygen (O_2), nitrogen (N_2), ammonia (NH_3) and noble gas—xenon (Xe) [37]. The most important thermodynamic parameters of these fluids are given in Table 2, where T, T_c denote the temperature

Table 2 Details on the phase equilibrium data for the systems considered in this article

Molecule	T_c (K)	ρ_c (kg m^{-3})	Range of data		
			T (K)	ρ_L (kg m^{-3})	ρ_V (kg m^{-3})
O_2	154.581	436.10	154.20–154.581	436.10–547.04	326.80–436.10
H_2	33.145	31.263	32.80–33.145	31.263–43.104	20.009–31. 263
N_2	126.192	313.30	125.80–126.192	313.30–400.79	228.20–313.30
NH_3	405.40	225.00	405.10–405.40	225.00–274.01	185.75–225.00
Xe	289.733	1100.00	289.40–289.733	1100.00–1319.5	909.41–1100.00

Table 3 Percentage values of *rms* errors of the VLE curve and critical densities between experimental, given by Eqs. (24)–(25) and (28)–(31) and equations in traditional parabolic shape (taken from [13]) data for test substances

rms %	Calc. from Eqs. (24–25)			Calc. from Eqs. (28–31)			Contained in [13]		
	ρ_L	ρ_V	ρ_c	ρ_L	ρ_V	ρ_c	ρ_L	ρ_V	ρ_c
O_2	4.61	4.28	0.021	4.57	2.97	0.028	5.07	4.92	0.29
H_2	8.78	9.48	0.023	2.89	2.65	0.031	3.23	3.25	0.43
NH_3	5.88	5.44	0.029	5.55	2.23	0.054	6.01	3.28	1.002
Xe	3.08	5.03	0.027	4.59	2.24	0.087	3.34	5.14	0.028
N_2	9.22	5.94	0.0044	1.80	4.22	0.023	10.52	7.28	0.95

and the critical temperature (expressed in Kelvin), $P,\ P_c$ denote the pressure and the critical pressure (expressed in Mega Pascal), $\rho_c,\ \rho_L,\ \rho_V$ denote the density–critical liquid and vapor, respectively (expressed in kilogram per cubic meter). The values of the critical parameters for all of tested substances were taken from [37]. The reason of choosing these data to analysis as well as the way of fitting calculated phase curves to real data is based on work [13].

The value of the asymptotic neighborhood of the liquid–vapor critical point was taken based on the expression of the scaled temperature-parameter $|t|$, which around the critical point not exceeds the value of $\sim 10^{-n}$. We assume that $|t| \sim k \times (10^{-4} \div 10^{-2})$ (where $k \in [1, 9]$) and corresponds to the temperature range of the interval $[T_c - 0.3\,\text{K}, T_c]$, where T_c is the critical temperature of the test substances.

The accuracy of the method described here was checked by comparing calculated values with the results of experimental data, giving in all the comparisons percentage *root-mean-square* deviations (% *rms*) (see Table 3)

$$\%\,rms = \sqrt{\frac{1}{N}\left[\sum_{i=1}^{N}\left(\frac{X_{exp} - X_{calc}}{X_{exp}}\right)^2\right]}$$

where X_{exp} are experimental values for the thermodynamic property of interest, X_{calc} are fitted values for the same property, and N is the number of data.

Table 3 lists the root-mean-square error deviations in density for the mentioned above $p\rho t$ data sets. We must note in this place, that comparison of the several data sets for selected fluids can be made only for data in the same ranges of temperatures (see adopted temperature range for analysis in Table 2).

3.1 Analysis of the behavior of the experimental data near the vapor–liquid critical point-discussion of results from numerical estimations

Semi qualitative description of the critical area and the prediction of the coexistence densities curves near the vapor–liquid critical point is a severe test for determined from calculation phase curves given by (24), (25), (28), (31). Is that because the nonanalytic nature of the asymptotic vicinity of the critical region means that most of the EOS can be expected to fail. We tried to avoid this conflict by applying to the calculation of so-called deviation parameters [see Eq. (1)] and order parameter for the VLE system [see Eq. (3) in Sect. 1].

In Fig. 1 we see that critical region of the coexistence curves is better reflected by phase curves determined from second method [see solid lines determined from Eqs. (28), (31)]. But for some fluids both methods gave very good, and qualitatively indistinguishable, results (compare Fig. 1(a, c, d) of liquid phase for xenon, oxygen and ammonia with Table 3). In addition the data obtained from second method for

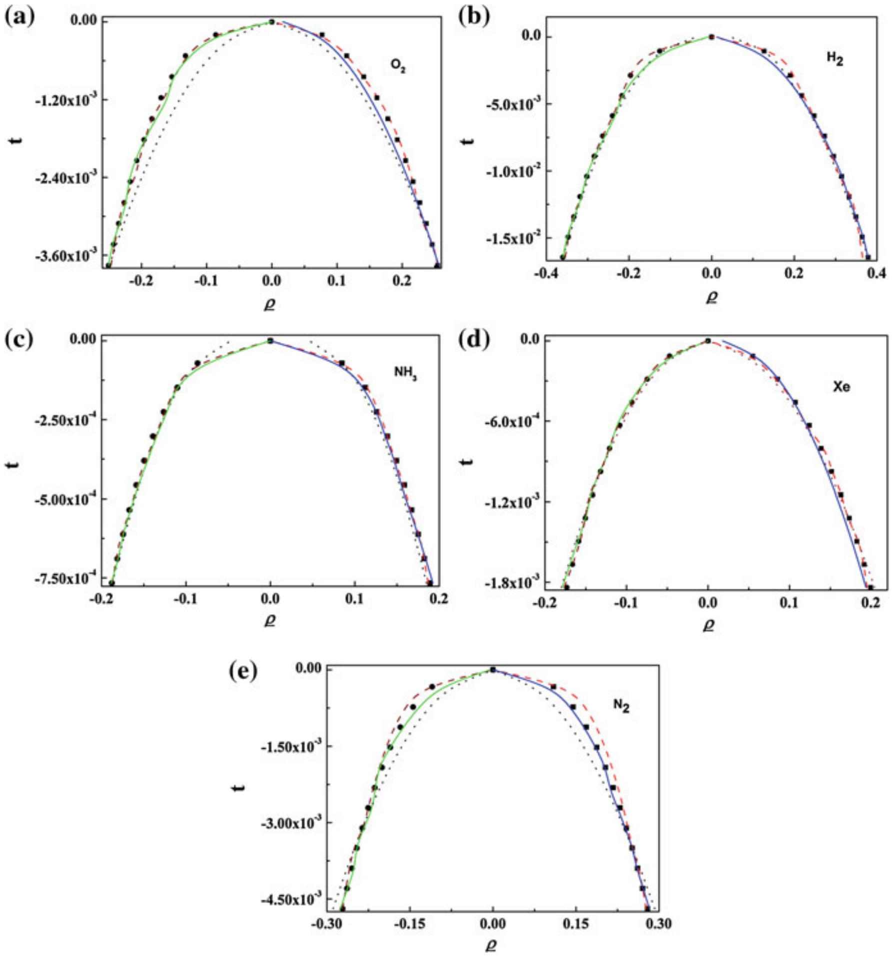

Fig. 1 Vapor–liquid critical point of the VLE curve determined from Eqs. (24)–(25) and (28)–(31) (where $\underline{\rho} = \tilde{\rho} = \rho/\rho_c - 1$, $t = T/T_c - 1$) and its comparison to experimental data taken from [37] (experimental data represents *black squares*—liquid phase, *black circles*—vapor phase, *lines* corresponds to data estimated by a theoretical approach for vapor phase from Eqs. (24), (28)—*wine dashed line* and *solid green line*, for liquid phase from Eqs. (25), (31)—*red dashed line* and *solid blue line*, respectively), **a** for oxygen, **b** for hydrogen, **c** for ammonia, **d** for xenon, **e** for nitrogen. The phase curves in *parabolic shape* is added for comparison (*dark grey dotted line*) (Color figure online)

vapor phase showing the tendency to rapid, local anomalies (see solid green line for nitrogen, xenon and oxygen on Fig. 1a, d, e), which confirm the nonanalytic nature of the critical region and the same problem determining the functional relationships for analyzed thermodynamic potential-density. Obviously, the above results are a consequence of the fact, that we excluded in our method the effect of molecular shape, other complicating factors, the influence of gravitational effects or the influence of dipole interactions. Hence some of these diatomic and polyatomic structures to pose a greater challenge for obtained from calculation phase curves and the outcomes are not quantitatively accurate. Results obtained from the first method characterize regularity and no significant deviations in compared with experimental data (especially for the both phase of oxygen, ammonia and hydrogen on Fig. 1a–c—see also similar percentage values of *rms* error in Table 3).

Another important distinction of the methods presented here is clearly visible “flattening” of the determined cubic phase curves near the critical point, which is typical for experimental systems and which is not include in the result based on the traditional parabolic form of the coexistence curve near the critical point suggested by VdW. The results obtained for example for ammonia, hydrogen and oxygen corroborate the cubic shape of the phase curves and have been compared with the parabolic shape of these curves [contrast dotted lines corresponding to the phase curves in parabolic shape [13] with dashed lines determined from Eqs. (24), (25) on Fig. 1a–c] as also prove that under certain assumptions, can be almost directly use the VdW EOS to obtain coexistence curves cubic shape, consistent with experiment (notice also higher percentage values of *rms* error in Table 3 for curves determined from equations in parabolic shape contained in [13]). Only in the case of xenon (Fig. 1d) these shapes of phase curves are qualitatively indistinguishable. Compare also the method presented by us to the results obtained by Weinberger [38].

One observes in Table 3 that, for analyzed fluids, first method after some mathematical transformations, gives very good approximation of real values of the critical density with value obtained from the method described here. In turn second method gives somewhat poorer values of the critical density in contrast to the real data (compare with each other solid lines on Fig. 1a–d) for hydrogen, nitrogen, ammonia or xenon with values of *rms* error in Table 3).

In Fig. 2a, we see that most of the results obtained from Eqs. (24) and (31) overestimated the liquid or vapor density of oxygen. Similar conclusion arises from Fig. 2e, where we notice that the results obtained from second method [i.e. from Eqs. (28) and (31)] overestimated the liquid and vapor density and underestimated densities obtained by first way [Eqs. (24) and (25)]. In turn in Fig. 2c one can observe that at high temperatures (lower values of parameter t), closer to the critical point, second way overestimated and first way underestimated the vapor density. In addition in Fig. 2a, b, e almost 100 % agreement (a zero line representing appropriate correlations by using the equations of Sect. 2, in all deviation plots) between selected values for the liquid and vapor density, far from the vicinity of the critical point, can be observed.

In sum, Fig. 2a–e show that the present models performed in a similar way, independently of the fluids being considered. For some substances the largest difference between the data is clear visible near the critical point [more than −14 % for the liquid density of nitrogen determined from Eq. (25) and more than −17 % for the vapor

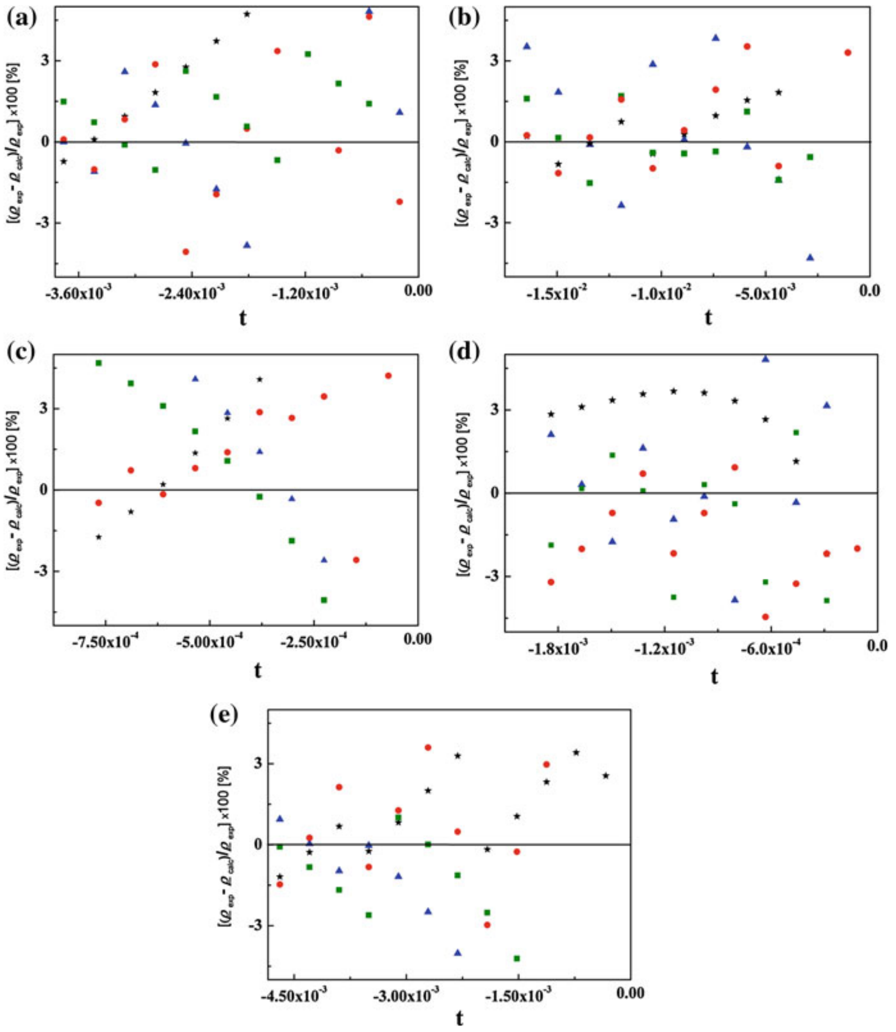

Fig. 2 Percentage density deviation (where $\underline{\rho} = \tilde{\rho} = \rho/\rho_c - 1, t = T/T_c - 1$) of the experimental $p\rho t$ data near the vapor–liquid critical point from values calculated from Eqs. (24)–(25) and (28)–(31) [*blue up triangle* and *black star* corresponds to liquid density determined from Eqs. (25), (31), *green square* and *red circle* corresponds to vapor density determined from Eqs. (24), (28)], **a** for oxygen, **b** for hydrogen, **c** for ammonia, **d** for xenon, **e** for nitrogen. *Black horizontal zero line* correspond to 100 % accuracy between the data. All data with deviations of more than ±5 % are plotted on the limit of the deviation scale (Color figure online)

density of hydrogen determined from Eq. (24)—points plotted on the limit of the deviation scale of Fig. 2b, e]. While the values of largest percentage deviation for the result obtained from Eqs. (28) and (31), at the critical point, amounted to just over −12 % for the liquid phase of xenon and almost 12 % for the vapor phase of nitrogen-points plotted on the limit of the deviation scale of Fig. 2(d, e).

Based on ways derived from this work, we see that the percentage value of *rms* error is lower when we use to analyze the second method and significantly increased, for some fluids, for the first method. Therefore, the error is strictly dependent on the applied method of calculation. Of course these values are radically different from the results obtained with accurate, multi parameter EOS. Other than the goal of this article was the straightforwardness of the model presented, but despite this fact the results presented here are, for some fluids, much better than the results obtained for example by Sadus [39] (especially for both phases of xenon and hydrogen, where author of this work used in analysis temperature range nearest to those chosen in this article).

We expect such a large distinction between the results obtained by adopting the VdW EOS in calculation than these contained in works [40,41]. It's obvious that the VdW EOS much better reflects the nature of the theoretical calculations than practical applications. Nevertheless we wanted show in this article that VdW EOS can be developed (at some assumptions) coexistence curves cubic shape and proved that VdW theory can also confirm not only the cubic shape but also predict the flatness of these curves. Moreover the impact on such divergent outcomes in comparison with other works, could also affect the critical exponent assumed value. This value, in real, for the selected fluids may slightly more than that adopted by us (compare for example experimental value of the critical exponent of oxygen [42] or xenon [43]).

4 Summary and conclusions

In this paper we have proposed a mathematical method for description the critical region of the VLE system. By using derived in [13] differential form of the coexistence densities curves and critical exponent theory we imported a nonlinear differential equations to linear form. We found their solution in a form of a cubic function, consistent with the considerations proposed by Levelt Sengers [28] and Guggenheim [29], Croxton [30], Wyczałkowska et al. [31], Weinberger and Schneider [32], Widom and Rice [33], Zimm [34]. Calculated in this way phase curves in cubic shape could be directly use for the semi qualitative description of the critical area (the critical value of one of the thermodynamic potential, density, is determined with accuracy do not exceeds of a few percent for both phases—liquid and vapor). The error, in general, was smaller for vapor density than liquid density. What is more we can estimate critical density with deviation not less than 0.0044 % for selected fluids (compare also this result with results contained in work of Nowak et al. [41]).

The generally good results obtained from Eqs. (24), (25), (28) and (31), indicate that the asymptotic VdW formula can be used as the basic for simple coexistence curves development. Thereby we have showed that under certain assumptions the VdW EOS as well confirm, on the basis of simple mathematical calculations, of cubic shape coexistence curve, consistent with experimental results, which to this day leads to conflict between the classical theory and experiment.

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