Asymmetry of the vapor–liquid coexistence curve: the asymptotic behavior of the “diameter”

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Abstract
We analyze, without resort to any model field-mixing scheme, the leading temperature-dependent term in the ‘diameter’ of the coexistence curve asymptotically close to the vapor-liquid critical point. For this purpose, we use a simple non-parametric equation of state which we develop by meeting several general requirements. Namely, we require that the desired equation (1) lead to correct asymptotic behavior for a limited number of the fluid’s parameters along selected thermodynamic paths, (2) reveal a Van der Waals loop below the critical point, and (3) be consistent with a rigorous definition of the isothermal compressibility in the critical region. For the temperature interval in question, the proposed equation approximates experimental data with an accuracy comparable to those given by Schofield’s parametric equation and by other authors’ equations. The desired term is obtained by applying the Maxwell rule to the equation and can be represented as $D_{2\beta} |\tau|^{2\beta}$, where $|\tau| = (T - T_c)/T_c$ and $\beta$ is the critical exponent for the order parameter. The amplitude $D_{2\beta}$ is determined explicitly for the volume–temperature and entropy–temperature planes.

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I. INTRODUCTION

The liquid–vapor critical point has recently attracted considerable interest in the context of liquid–vapor asymmetry in near-critical fluids [1–4]. This asymmetry manifests itself as a deviation of the temperature behavior of the "diameter" of the coexistence curve, $d \equiv (\rho_1 + \rho_2)/2\rho_c$, from the critical isochore $\rho = \rho_c$. Here $\rho_1$ and $\rho_2$ are the densities of liquid and saturated vapor for a given temperature $T$, and $\rho_c$ is the critical density. The first empirical evidence of this fact was obtained by Callen and Mathias [3], who suggested a linear behavior of $d$ with $T$ as the critical temperature $T_c$ is approached: $d = 1 + D_1 |\tau|$, where $\tau \equiv (T - T_c)/T_c$ is the reduced distance from $T_c$ and $D_1$ is a constant. This relation is known as the “law” of the rectilinear diameter. The later theoretical investigations [4–8] and then [1–4] revealed certain deviations from this law, which can be described with two additional nonanalytic terms, proportional to $|\tau|^{1-\alpha}$ and $|\tau|^{2\beta}$, $\alpha$ and $\beta$ being the critical exponents for the heat capacity at constant volume $C_V$ and the order parameter respectively:

$$d = 1 + D_{2\beta} |\tau|^{2\beta} + D_{1-\alpha} |\tau|^{1-\alpha} + D_1 |\tau| + \ldots \ (1)$$

For fluids, $1 - \alpha > 2\beta$, and the first temperature-dependent term on the right of Eq. (1) is expected to dominate in the region asymptotically close to the critical point. Since the extrapolation of $d$ to the critical temperature is commonly used to obtain the critical density, the determination of this term becomes of great practical importance.

Theoretically, Eq. (1) is usually justified by starting from scaling theory, dealing with two independent scaling fields, $h_1$ and $h_2$, and two conjugate scaling densities, $A_1$ and $A_2$. The critical part of the thermodynamic potential is taken to be a homogeneous function of $h_1$ and $h_2$. The form of the scaling function and the values of $\alpha$ and $\beta$ for a particular model can, in principle, be calculated by using the renormalization group approach and $\varepsilon$–expansion. For all models of the same class of universality, these quantities are identical. In particular, fluids are often treated in terms of the lattice-gas model, which is isomorphic to the Ising model. However, this statement is approximate, for the Ising model has perfect symmetry with respect to the change of sign of the quantities $h_1$ and $A_1$, which real fluids lack. As a result, the coexistence curve within this model is symmetrical (the constants $D$ in Eq. (1) are zero). In order to describe the critical point of real fluids and account for asymmetry of the liquid–vapor coexistence curve, various field-mixing schemes have been proposed (see Ref. [9, 10] and further developments [11, 12]), within which independent physical fields (say, the chemical potential and temperature) and the conjugate physical densities (the density and entropy) are represented as linear combinations of the scaling fields ($h_1$ and $h_2$) and densities ($A_1$ and $A_2$) of the symmetric model.

Besides solving the problems of the proper choice of the order parameter, the conjugate field, the form of the scaling function, etc., which are difficult in themselves,
practical implementation of field-mixing schemes implies the use of certain model assumptions of both the form of the mixing and the numerical values of the asymmetry coefficients in the corresponding linear combinations. In practice, these coefficients and, consequently, the coefficients $D$ in Eq. (1) serve as adjustable parameters. The extraction of their numerical values from experimental data is a very difficult task in itself (see the discussion of this matter in [4]), due to the difficulties associated with carrying out experiment in the critical region and the problem of separation of different terms in Eq. (1).

In view of the above-said, the question arises of whether there is an alternative way of justifying Eq. (1), which would allow definite conclusions on the universality of separate terms in Eq. (1) and estimations of their coefficients. In the present communication, we report the results of study of the leading temperature-dependent terms in $d$ which were obtained without resort to any model field-mixing scheme. Namely, we proceed from the idea [11] that an efficient equation of state for the asymptotic neighborhood of the liquid–vapor critical point can be developed by using information on the asymptotic behavior of a limited number of the parameters of the fluid along selected thermodynamic paths. The original approach [11] is modified in several directions. Firstly, we expand the set of the fluid’s parameters used to construct the desired equation. Secondly, we take into account a rigorous definition of the isothermal compressibility in the critical region: this definition becomes a source of asymmetry of the coexistence curve. Thirdly, we require that for $\tau < 0$, the desired equation reveal a typical Van der Waals loop. Having met these requirements, we obtain the desired equation and then test it for the accuracy of interpolation of experimental data. The sought-for asymptote of $d$ is determined in the explicit form by applying Maxwell’s rule to the equation. Finally, we analyze the behavior of the diameter in the entropy–temperature plane.

II. CONSTRUCTION OF THE EQUATION OF STATE

In his work [11], Martynov developed a simple equation of state for critical fluid by using the asymptotic law for entropy–temperature plane. In view of the above-said, the question arises of whether there is an alternative way of justifying Eq. (1), which would allow definite conclusions on the universality of separate terms in Eq. (1) and estimations of their coefficients. In the present work, we expand the original set (2), (3) to incorporate the well-known fact that the derivative $(\partial \pi / \partial \tau)_\omega$ remains finite along the critical isochore, including the critical point itself (see, for instance, Ref. [10]). Consequently, we additionally require that desired equation satisfy the relation

$$
\left( \frac{\partial \pi}{\partial \tau} \right)_\omega = M = \text{const as } \tau = 0 \text{ and } \omega = 0. \tag{4}
$$

Also, we pay attention to the fact that the rigorous definition of $\beta_T$ in terms of $\pi$, $\tau$, and $\omega$ is written as

$$
\beta_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_{NT} = -\frac{1}{1 + \omega} \frac{1}{P_c} \left( \frac{\partial \omega}{\partial \tau} \right)_\tau = -\frac{1}{P_c} \left( \frac{\partial \ln(1 + \omega)}{\partial \pi} \right)_{\tau}. \tag{5}
$$

Eq. (5) is asymmetric with respect to the transformation $\omega \to -\omega$, but this source of asymmetry, to our best knowledge, has never been given an in-depth analysis.

With postulates [2]–[5], we begin our consideration with the region $\tau > 0$. Following reasoning [11], we note that Eq. (3) is actually the equation of state valid only for the curve $\tau = 0$. As we shift from the latter, the desired equation takes the form $\pi(\tau, \omega) = \pi(0, \omega) + f(\tau, \omega)$, where the unknown function $f(\tau, \omega)$ is expected to vanish at $\tau = 0$ and to satisfy Eqs. (2), (4) and (5). It follows that

$$
\pi(\tau, \omega) = M\tau - \frac{1}{\Gamma_0} \ln(1 + \omega) \tau^\gamma - D_0\omega|\omega|^{\delta-1}, \quad \tau > 0. \tag{6}
$$

For the classical values of the exponents $\gamma = 1$, $\delta = 3$ and amplitudes $\Gamma_0 = 1/6$, $D_0 = 3/2$, and for the value $M = 4$, Eq. (6) coincides with the asymptotic form of the Van der Waals equation for $\tau$, $\omega << 1$: $\tau = 4\tau - 6\omega\tau - (3/2)\omega^3 + ...$. Next, we suggest that below the critical temperature ($\tau = -|\tau| < 0$), Eq. (6) must be generalized so as to demonstrate a typical Van der Waals loop and transform, for the corresponding values of the exponents and amplitudes, to the asymptotic form of the Van der Waals equation for $|\tau|$, $\omega << 1$: $\tau = -4|\tau| + 6\omega|\tau| - (3/2)\omega^3 + ...$. Then

$$
\pi(\tau, \omega) = -M|\tau| + \frac{1}{\Gamma_0} \ln(1 + \omega)|\tau|^\gamma - D_0\omega|\omega|^{\delta-1}, \quad \tau < 0. \tag{7}
$$

Combined together, Eqs. (6) and (7) give

$$
\pi(\tau, \omega) = M\tau - \frac{1}{\Gamma_0} \ln(1 + \omega)\tau |\tau|^{\gamma-1} - D_0\omega|\omega|^{\delta-1}. \tag{8}
$$
Eq. (8) represents the desired equation and forms the basis for further analysis.

III. TESTING THE EQUATION OF STATE

In the quadratic approximation in \( \omega \), \( \ln(1 + \omega) \approx \omega - \omega^2/2 \), and Eq. (8) almost coincides with the equation obtained in Ref. [12], except for terms of order \( \omega^{3+1} \) and \( 1/\omega^{2-\alpha} \). In its accuracy, the latter proves to be comparable with Schofield’s parametric equation.

Here, we consider a more sophisticated way of testing Eq. (8), hinted by the suggestion that the law of corresponding states can be extended to the asymptotic neighborhood of the liquid–vapor critical point. If so, then the variables \( \pi, T, \omega \) can be properly normalized so as to fall on one and the same curve. For Eq. (8), the form of this curve is particularly suitable for processing, with only one adjustable parameter actually used.

The presence of the logarithmic factor in Eq. (8) makes the choice of the normalized variables simple. After we set
\[
p = \frac{\pi}{D_0}, \quad t = \frac{T}{(D_0 V_0)^{1/\gamma}}, \quad v = \omega,
\]
Eq. (8) takes the form
\[
p(t, v) = at - \ln(1 + v) t |\gamma^{\gamma - 1} - v|^{\delta - 1},
\]
where \( a \) is a constant. If the law of corresponding states does occur for a certain class of near-critical fluids, \( a \) remains the same for all members of the class. In particular, the Van der Waals and Dieterici equations give estimates \( a = 2/3 \) and \( a = 3/4 \) respectively.

To test the validity of Eq. (10) for interpolation of \( \rho T \) data in the close vicinity of the critical point, we used data for water [14, 15], nitrogen [16], and carbon dioxide [17]. The values of the critical exponents for all the substances were taken to be equal to their values in the three-dimensional Ising model: \( \gamma = 1.239, \delta = 4.80 \) [18]. The critical amplitudes were calculated by using the values of the parameter \( z = P_c V_c / RT_c \) and approximation formulas [19]. The parameters of the critical points were taken from the original works [14, 17].

To scrutinize the functional form of Eq. (10), the values of the function \( f = p + \ln(1 + v) t |\gamma^{\gamma - 1} - v|^{\delta - 1} \) were plotted for available values of the variables [9], and then the possibility of their interpolation with a straight line at was analyzed (see Figs. 1 and 2, where \( \Delta \rho \equiv \rho - \rho_c \)). The \( f \) versus \( t \) dependence was indeed found to approach a linear one as the density interval was narrowed. The slope \( a \) of the interpolation line was determined with the least square procedure and then used to estimate the root-mean-square error \( \Delta \rho = \sqrt{N^{-1} \sum_{i=1}^{N} (P_{\exp} - P_{\text{theor}}) / P_{\exp}}^2 \) for direct approximation of the \( \rho T \)-data with the original equation

![Graphs showing data fitting for Eq. (8)](attachment:image)

**FIG. 1:** \( f \) versus \( t \) in the region \(-2.472 \times 10^{-4} < \tau < 1.236 \times 10^{-3}, \ -0.3 \leq \Delta \rho \leq 0.3 \) according to data [14, 15] for water (a) and its asymptotic behavior for \(-0.15 \leq \Delta \rho \leq 0.15 \) (b); \( a = 0.63 \) and \( \Delta \rho = 0.27\% \).

![Graphs showing data fitting for Eq. (8)](attachment:image)

**FIG. 2:** \( f \) versus \( t \) in the region \(-1.236 \times 10^{-3} < \tau < 3 \times 10^{-3}, \ -0.23 \leq \Delta \rho \leq 0.23 \) according to data [16] for nitrogen (a) and its asymptotic behavior for \(-0.15 \leq \Delta \rho \leq 0.15 \) (b); \( a = 0.48 \) and \( \Delta \rho = 0.4\% \).

IV. THE COEXISTENCE CURVE

Let \( V_1 \) and \( V_2 \) be the maximum and minimum molar volumes (for a given \( \tau \)) of the coexisting liquid and vapor respectively, and let \( \omega_1 = (V_1 - V_c) / V_c = -|\omega_1| \) and \( \omega_2 = (V_2 - V_c) / V_c = \omega_2 > 0 \) be the corresponding values of \( \omega \). It is well-known (see, for example, [20]) that the form of the coexistence curve can be determined from the equality of the chemical potentials for the coexisting phases, or, equivalently, from Maxwell’s rule.

Below the critical point, the liquid \( (\omega \leq \omega_1) \) and vapor \( (\omega \geq \omega_2) \) phases satisfy Eq. (8). In particular, for the values \( \omega_1 \) and \( \omega_2 \) on the coexistence curve we have:
\[
\pi(\tau, \omega_1) = -M |\tau| + \frac{1}{\Gamma_0} \ln(1 + |\omega_1|) |\tau|^{\gamma} D_0 |\omega_1|^{\delta}, \quad (11)
\]
\[
\pi(\tau, \omega_2) = -M |\tau| + \frac{1}{\Gamma_0} \ln(1 + \omega_2) |\tau|^{\gamma} - D_0 |\omega_2|^{\delta}. \quad (12)
\]
For the two-phase region \((\omega_1, \omega_2)\), Eq. (3) must be corrected according to Maxwell’s rule:

\[
\int_{\omega_1}^{\omega_2} \pi(\tau, \omega) \, d\omega = \bar{\pi}(\omega_2 - \omega_1),
\]

where \(\bar{\pi}\) is the constant pressure along the isotherm–isobar \((\omega_1, \omega_2)\). At the endpoints of this segment, \(\bar{\pi}\) is equal to the values given by (11), (12): \(\bar{\pi} = \pi(\tau, \omega_1) = \pi(\tau, \omega_1)\).

Taking the integral (13) and combining the result with Eqs. (11) and (12), we find:

\[
\frac{1}{\Gamma_0} |\tau|^\gamma \ln (1 + \omega_2) - \ln (1 - |\omega_1|) = D_0 \left(\omega_2^\delta + |\omega_1|^\delta\right),
\]

(14)

\[
\frac{1}{\Gamma_0} |\tau|^\gamma (\omega_2 + |\omega_1|) = \frac{\delta}{\delta + 1} D_0 \left(\omega_2^\delta + |\omega_1|^\delta\right) + D_0 \left(\omega_2^\delta + |\omega_1|^\delta\right).
\]

(15)

Thus, the analysis of the coexistence curve reduces to the study of the system of Eqs. (14), (15). To obtain the shape of this curve, we define a nonnegative quantity \(x\) by the relation

\[
\omega_2 = x|\omega_1|,
\]

(16)

and then divide both sides of Eqs. (14), (15) into each other to eliminate the variable \(\tau\). As a result, we see that \(x\) is the only root of the transcendental equation

\[
\left[ \frac{\delta}{\delta + 1} |\omega_1| (x^{\delta+1} - 1) + (x^\delta + 1) \ln \frac{1 + |\omega_1|x}{1 - |\omega_1|} - |\omega_1| (x^\delta + 1) (x + 1) \right] = 0,
\]

(17)

with \(|\omega_1|\) being a parameter. For a fixed value of \(|\omega_1|\) and near the point \(x = 1\), the left side of Eq. (17) is a monotone increasing function of \(x\). The single root of this function is close to unity and is located in the region \(x < 1\).

To obtain the analytical solution of the system (14), (15), we represent \(x = 1 + \varepsilon\), where \(\varepsilon \ll 1\). In the linear approximation with respect to \(\varepsilon\), Eq. (17) gives

\[
\varepsilon = \frac{4|\omega_1| \left(1 - \frac{1}{2|\omega_1|} \ln \frac{1 + |\omega_1|}{1 - |\omega_1|}\right)}{\delta (1 + |\omega_1|) \ln \frac{1 + |\omega_1|}{1 - |\omega_1|} - 2|\omega_1| \left(\delta + 1 - \frac{1}{1 + |\omega_1|}\right)}.
\]

(18)

Expanding the logarithmic functions on the right of Eq. (18) in power series with respect to \(|\omega_1|\) and restricting ourselves to the linear approximation, we find \(\varepsilon = 0\) and \(\omega_2 = |\omega_1|\). Eq. (14) then immediately gives the well-known asymptotic law

\[
\omega_2 = -\omega_1 = B_0 |\tau|^\beta + o \left(|\tau|^\beta\right),
\]

(19)

with amplitude

\[
B_0 = \frac{1}{(D_0 \Gamma_0)^{1/(\delta - 1)}}.
\]

(20)

In the second-order approximation with respect to \(|\omega_1|\), these two relations still hold. Asymmetry of the coexistence curve appears only within the third-order approximation, in which case we find that asymptotically close to the critical point,

\[
\varepsilon = \frac{2|\omega_1|}{3(\delta - 1)} + O \left(|\omega_1|^2\right),
\]

(21)

\[
\omega_2 - \omega_1 = 2B_0 |\tau|^\beta + O \left(|\tau|^\beta\right),
\]

(22)

\[
\omega_2 + \omega_1 = \varepsilon |\omega_1| = -\frac{2}{3(\delta - 1)} B_0^2 |\tau|^{2\beta} + o \left(|\tau|^{2\beta}\right).
\]

(23)

It follows from Eq. (23) that the desired asymptotic expression for the “diameter” of the coexistence curve in the volume–temperature plane is

\[
d_V = \frac{V_1 + V_2}{2V_c} = 1 - \frac{1}{3(\delta - 1)} B_0^2 |\tau|^{2\beta} + o \left(|\tau|^{2\beta}\right).
\]

(24)

V. THE ENTROPY–TEMPERATURE PLANE

Incorporating an additional requirement (11) on the asymptotic behavior of the molar heat capacity \(c_V(\tau, \omega)\) along the critical isochore \(\omega = 0\) in the two-phase region,

\[
c_V(\tau, 0) = A_0 |\tau|^{-\alpha} + \ldots \text{ as } \tau \to 0^-,
\]

(25)

let us determine the “diameter” \(d_s = (s_1 + s_2)/s_c\) of the coexistence curve in the entropy–temperature plane. For
this purpose, we first use the relation \(d\mu = -s dT + V dP\), \(s\) and \(V\) being the molar entropy and volume of the system, to find the chemical potential \(\mu\). In terms of \(\tau\), \(\omega\), and \(\pi\), and for a constant temperature, we have

\[
(d\mu)_{\tau} = V_c P_c (1 + \omega) (d\pi)_{\tau}.
\]

(26)

Correspondingly,

\[
\mu(\tau, \omega) = V_c P_c \left( \pi + \int \omega \ d\pi \right) + f(\tau),
\]

(27)

where the integral is taken along an isotherm and \(f(\tau)\) is a function of temperature alone. In view of Eq. (28), we find

\[
\mu(\tau, \omega) = P_c V_c \left[ M \tau - \frac{1}{\Gamma_0} \omega \tau |\tau|^{\gamma-1} - D \omega |\omega|^{\delta-1} - D_0 \frac{\delta}{\delta + 1} |\omega|^{\delta+1} \right] + f(\tau).
\]

(28)

In the asymptotic vicinity of the critical point, the fourth term in the brackets can be neglected, and Eq. (28) takes the form

\[
\frac{\mu(\tau, \omega) - \mu(\tau, 0)}{P_c V_c} = -\omega |\omega|^{\delta-1} h \left( \tau / |\omega|^{1/\beta} \right),
\]

(29)

in accordance with the scaling hypothesis [21]. The asymptote of the scaling function \(h(x)\) for \(x \ll 1\) is \(h(x) = D_0 + \frac{1}{10} x^7\). Implicitly present in Ref. [11], this form of the scaling function was later postulated in Ref. [12]. The omitted term in the brackets in Eq. (28) represents, evidently, the first correction to the asymptotic law (29).

As a check on the validity of Eq. (28), we can easily verify that the phase-equilibrium conditions for two coexisting phases with molar volumes \(\omega_1 = -|\omega_1|\) and \(\omega_2\) \((\tau < 0)\),

\[
\pi(\tau, \omega_1) = \pi(\tau, \omega_2), \quad \mu(\tau, \omega_1) = \mu(\tau, \omega_2),
\]

(30)

reduce to Eq. (12) and (13), provided, as was already suggested, that \(f(\tau)\) is independent of \(\omega\).

In view of Eq. (28), the molar entropy,

\[
s = -\frac{1}{T_c} \frac{\partial \mu}{\partial \tau} \bigg|_{\pi} = \frac{P_c V_c}{T_c} (1 + \omega) \frac{\partial \pi}{\partial \tau} \bigg|_{\omega} - \frac{1}{T_c} \frac{\partial \mu}{\partial \tau} \bigg|_{\omega},
\]

(31)

is given by

\[
c_v(\tau, \omega) = \frac{P_c V_c}{T_c} \frac{1}{\Gamma_0} [\omega - (1 + \omega) \ln (1 + \omega)]
\]

\[
\times \gamma |\tau|^\gamma - 1 - \frac{1 + \tau}{T_c} f''(\tau).
\]

(34)

If, according to Eq. (25),

\[
\frac{P_c V_c}{T_c} \gamma (\gamma - 1) B_0^2 \frac{1 + 1 + \tau}{T_c} f''(\tau) = A_0 |\tau|^{-\alpha} + \ldots,
\]

(35)

then, taking into account that the critical value of the entropy \(s_c = s(0, 0) = -f'(0)/T_c\), we find

\[
\frac{s(\tau, \omega)}{T_c} = \frac{P_c V_c}{T_c} \left( M \omega + \frac{\gamma}{\Gamma_0} [\omega - (1 + \omega) \ln (1 + \omega)] |\tau|^\gamma - 1 \right)
\]

\[
+ \int_0^\tau \left\{ \frac{A_0}{1 + \tau} - \frac{P_c V_c (\gamma - 1) B_0^2}{2 \Gamma_0} |\tau|^\gamma - 1 + o (|\tau|^{-\alpha}) \right\}
\]

\[
+ s_c,
\]

(36)

whence

\[
ds = 1 - \frac{P_c V_c}{T_c} \frac{M B_0^2}{3 (\delta - 1)} T_c |\tau|^{2\beta}
\]

\[
- \frac{1}{s_c (1 - \alpha)} \left( A_0 + \frac{P_c V_c \beta \gamma B_0^2}{T_c \Gamma_0} \right) |\tau|^{1-\alpha} + o (|\tau|^{-\alpha}).
\]

(37)

It follows that condition (25) is not necessary to explain the appearance of the \(|\tau|^{2\beta}\) term in the “diameter” (37). On the other hand, Eq. (34) shows that on both branches of the coexistence curve, \(c_v\) diverges as \(|\tau|^{-\alpha}\) as the critical point is approached from below.

VI. CONCLUSION

The temperature behavior of the “diameter” of the coexistence curve in the asymptotic vicinity of the vapor–liquid critical point has been studied within a model-free approach, based upon general thermodynamic definitions and relationships. The critical exponent of the leading temperature-dependent term in the diameter is found to be \(2\beta\). The critical amplitude for this term is determined explicitly for the volume–temperature and entropy–temperature planes. In the latter case, the “\(1 - \alpha\)” term has been recovered as well.
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