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Coexistence Curve Equation for Several One-Component Fluids in the Vicinity of the Critical Point[1]

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Based on the available literature data on the temperature dependence of coexisting densities near the critical point for Ne, HD, N_2, and C_2H_4, the disadvantages of using the extended scaling equation of the coexistence curve with the Ising exponent are shown. Combined statistical methods are proposed to reanalyze these data. For all the above-mentioned substances, in the range of reduced temperature $1.3 \times 10^{-4} < \tau < 6 \times 10^{-3}$ to 2×10^{-2}, we obtain for the order parameter a single-term fit, with the common value $\beta = 0.355$. The fit describes the experimental densities with an uncertainty of 0.06 to 0.1%.

KEY WORDS: coexistence curve; critical exponents; critical point; Ising model; scaling laws; universality classes.

1. INTRODUCTION

It is generally accepted that precise experimental data for fluids near the critical point may be well fitted by scaling equations with Ising critical exponents. This conclusion is supported in particular by accurate heat capacity and light scattering data. But in application of the power laws with the Ising critical exponent to the coexistence curve of one-component fluids, it is necessary to include a sufficient number of correction terms [1]. We draw attention to the disadvantages of using the extended scaling equations with the Ising exponent β for describing coexistence curves of simple

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one-component fluids. The methods of statistical analysis of coexisting vapor and liquid densities [2–5] are applied to get a more accurate and useful representation.

2. CALCULATIONS

We selected the available experimental data from Ref. 6 on the temperature dependence of coexisting densities of C_2H_4, N_2, Ne, and HD. In Ref. 7 these data were approximated by Wegner expansions:

$$\begin{aligned}\Delta\rho_s &= (\rho_l - \rho_g)(2\rho_c)^{-1} \\ &= B_\beta \tau^\beta + B_{\beta+\Delta}\tau^{\beta+\Delta} + B_{\beta+2\Delta}\tau^{\beta+2\Delta} + \dots \end{aligned} \tag{1}$$

$$\begin{aligned}\Delta\rho_d &= (\rho_l + \rho_g)(2\rho_c)^{-1} - 1 \\ &= A_0 + A_{1-\alpha}\tau^{1-\alpha} + A_{1-\alpha+\Delta}\tau^{1-\alpha-\Delta} + \dots \end{aligned} \tag{2}$$

where ρ_l and ρ_g are the liquid and vapor densities, $\tau = (T_c - T)/T_c$, ρ_c, and T_c are the critical density and temperature, respectively, and A_i and B_i are adjustable coefficients. The critical exponents were fixed and were equal to

$$\beta = 0.325 \dots 0.327, \qquad \Delta = 0.5, \qquad 1 - \alpha = 0.89 \tag{3}$$

In our opinion, Eqs. (1) and (2) with exponents given by Eq. (3) raise serious objections. Mainly, the residuals from the descriptions of the experimental data by the first terms in Eq. (1) for Ne, N_2, and C_2H_4 indicate that such a leading term does not describe any experimental point. For example, the fit of the experimental data for N_2 obtained in Ref. 7 is discussed. The temperature dependence of the coxistence densities of N_2 was fitted in Ref. 7 by a three-term power law (1) with a critical exponent given by Eq. (3) in the temperature range $1.8 \times 10^{-2} > \tau > 4.0 \times 10^{-4}$. The residuals of the fit of the experimental data by the leading term, by the leading and the first correction terms and, by the leading and the two correction terms,

$$S = \Delta\rho_s - 1.478\tau^{0.3253} \tag{4}$$

$$S = \Delta\rho_s - 1.478\tau^{0.3253} - 1.56668\tau^{0.8253} \tag{5}$$

$$S = \Delta\rho_s - 1.478\tau^{0.3253} - 1.56668\tau^{0.8253} + 3.0742\tau^{1.3253} \tag{6}$$

are shown in Fig. 1.

Obviously, not only the leading term but also the leading and the first correction terms are unable to fit adequately any partial temperature range

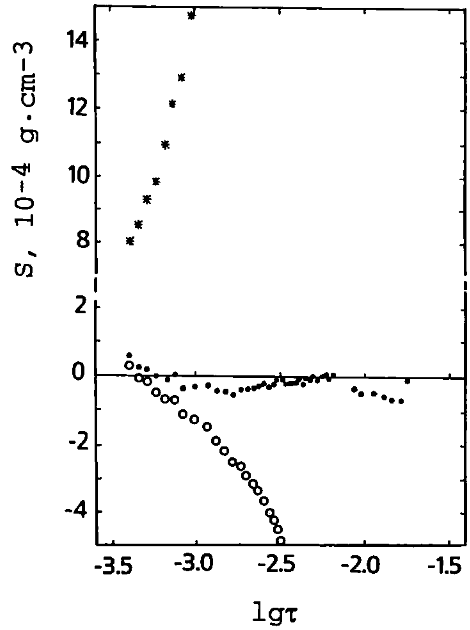

Fig. 1. Residuals S of approximation of the experimental data for N_2 by the leading term [Eq. (4); $*$], by the leading and first correction terms [Eq. (5); ○], and by the leading and two correction terms [Eq. (6); ●], with the exponents and amplitudies, presented in Ref. 7.

near the critical point. The analysis of residuals for other fits obtained in Ref. 7 leads to the same conclusion. So the asymptotic region (where the contribution of corrections $B_{\beta+\Delta}\tau^{\beta+\Delta}$, $B_{\beta+2\Delta}\tau^{\beta+2\Delta}$,..., does not exceed the experimental error) is found to be much closer to the critical point than the experimentally accessible temperature range $\tau > 10^{-4}$.

The main assumption of our treatment is that the asymptotic region is within the experimentally attainable temperature interval. We have endeavored in this research to determine β_0 and other exponents directly from the experimental data. For this purpose the data were fitted by the equations

$$\Delta\rho_s = B_0\tau^{\beta_0} + B_2\tau^{\beta_2} + B_4\tau^{\beta_4} + \ldots \tag{7}$$

$$\Delta\rho_d = B_1\tau^{\beta_1} + B_3\tau^{\beta_3} + \ldots \tag{8}$$

where exponents β_i and coefficients B_i are adjustable parameters.

The total uncertainty of the density measurements in Ref. 6 was estimated as $(2\text{–}3)\times 10^{-4}\,\mathrm{g\cdot cm^{-3}}$, but the accuracy of experimental determination of the critical parameters T_c and ρ_c was not mentioned. Thus, in Ref. 7 the values o T_c and ρ_c were selected during the fitting of the experimental data. Hence in the present paper the critical parameters T_c and ρ_c were also refined during the fitting.

The following three criteria were used for choosing a correct description for the experimental data. The first criterion concerns the independence of the critical exponents from the interval of the fit in the asymptotic regions for both β_0 and β_1. The second criterion involves the minimization of the residual sum-of-squares S of the fit for varying values of the critical parameters. The third criterion deals with the analysis of the temperature dependence of the scaling function:

$$|\psi_{1,g}| = |(\rho_{1,g}-\rho_c)/(\rho_c\tau^{\beta_0})| = |\pm\Delta\rho_s+\Delta\rho_d|\,\tau^{-\beta_0} \tag{9}$$

We discuss these criteria in detail.

The first criterion for the determination of the value of critical exponent β_0 is that the critical exponent be independent of the interval of the fit. For example, Fig. 2 shows the temperature dependence of the effective

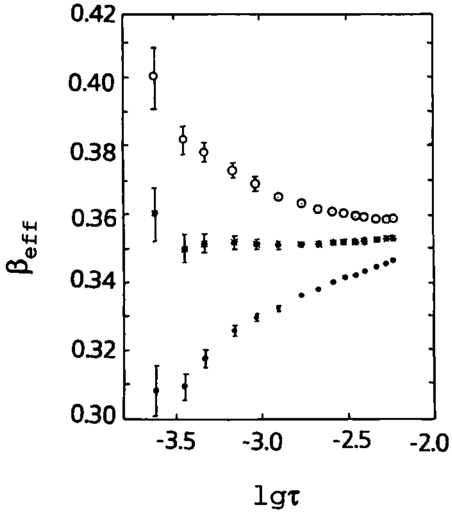

Fig. 2. Temperature dependence of the effective exponent β_{eff} for the coexistence curve of HD, fitted by a one-term power law [Eq. (10)] in different temperature intervals, and for T_c = 35.9585 (○), 35.9578 (∗), and 35.9569 (●) K.

values of the critical exponent β_{eff} obtained by fitting the experimental data for HD by a single-term power law with amplitude B_{eff}:

$$\Delta\rho_s = B_{\mathrm{eff}}\tau^{\beta_{\mathrm{eff}}} \tag{10}$$

in partial temperature ranges formed by progressively omitting, one point at a time, the data point farthest from T_c. It is shown in Fig. 2 that at $T_c = 35.9578$ K, the exponent $\beta_0 = 0.352 + 0.001$ is independent of the approximation interval within the limits of random error. For other values of T_c, a curvature is observed as the critical point is approached. Similar conclusions can also be drawn about the behavior of the coexistence curves of Ne, N_2, and C_2H_4.

Our T_c and β_0 values are also supported by Fig. 3, which shows the dependence of β_{eff} on the choice of T_c for three different sets of experimental data for Ne. It can be seen from Fig. 3a that all three curves intersect at a single point corresponding to $\beta_{\mathrm{eff}} = \beta_0 = 0.3575$ and $T_c = 44.481$ K.

The same figure also illustrates the second criterion used by us, namely, the fact that the minimum value of the statistical criterion χ^2 [8],

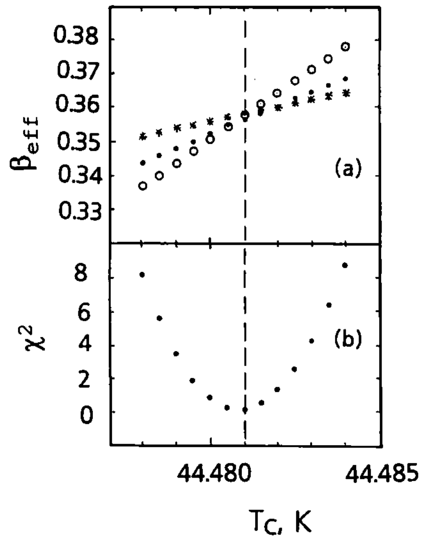

Fig. 3. (a) Dependence of β_{eff} on T_c according to Eq. (10) for Ne in three temperature ranges: $43.769 < T < 44.45$ K (*), $44.241 < T < 44.45$ K (○), and $44.394 < T < 44.45$ K (●). (b) Plot of χ^2 vs T_c for approximation of the experimental data in the temperature range $44.241 < T < 44.45$ K.

Table I. Results of Fits of Eq. (7) with One Term

Substance/ number of exp. points	Temperature interval (K) (reduced temperature)	β_0	B_0	$T_{c'}$ (K)	ΔT_c (K)
C_2H_4/35	276.8537 – 282.2766 (1.96×10^{-2}–3.55×10^{-4})	0.355	1.937	282.384	+0.009
Ne/19	42.4825–44.45 (2.28×10^{-2}–7.0×10^{-4})	0.3575	1.7973	44.481	+0.002
HD/31	35.7460–35.9532 (5.89×10^{-3}–1.3×10^{-4})	0.352	1.5929	35.9578	+0.0008
N_2/42	123.9683–126.1637 (1.8×10^{-2}–4.0×10^{-4})	0.355	1.8340	126.220	+0.0057

associated with the residual sum-of-squares, also corresponds to $T_c = 44.481$ K and $\beta_{\text{eff}} = \beta_0 = 0.3575$ (Fig. 3b).

Such analysis was performed for the experimental data for Ne, HD, N_2, and C_2H_4 and gave similar results, which are presented in Table I. In the sixth column in Table I, the temperature differences ΔT_c are listed and they indicate how much the values $T_{c'}$, obtained in our approximation, differ from T_c values used in Ref. 7 for the fit by Eq. (1) with β_0 in the range of 0.325 to 0.3272. It is seen from Table I that an increase in T_c by values from 0.0008 to 0.009 K leads to the same β_0 values for all four substances: $\beta_0 = 0.355 + 0.003$, which is similar to β_0 obtained earlier in our laboratory for C_6H_6 [9], C_5H_{12} [10], C_7H_{16} [11], and other substances [12–14].

The third criterion is necessary for the control of the correctness of the critical exponent β_0 determination. According to modern concepts of the critical behavior of a substance an asymptotic temperature range must exist close to the critical point. If the value β_0 is determined correctly and it corresponds to experimental data the scaling function $|\psi_{1,g}|$ has the form

$$\begin{aligned} |\psi_{1,g}| &= |(\rho_{1,g} - \rho_c)/(\rho_c \tau^{\beta_0})| \\ &= |\pm B_0 + B_1 \tau^{\beta_1 - \beta_0} \pm B_2 \tau^{\beta_2 - \beta_0} + \ldots| \end{aligned} \tag{11}$$

But if the critical exponent of the coexistence curve is incorrect (let us mark it as β_*), the form of scaling function $\psi_{1,g}$ will be another:

$$\begin{aligned} |\psi_{1,g}| &= |(\rho_{1,g} - \rho_c)/(\rho_c \tau^{\beta_*})| \\ &= |\pm B_0 \tau^{\beta_0 - \beta_*} + B_1 \tau^{\beta_1 - \beta_*} \pm B_2 \tau^{\beta_2 - \beta_*} + \ldots| \end{aligned} \tag{12}$$

The exponent of the leading term in Eq. (12) may be positive, negative, or equal zero. If $\beta_* < (>) \beta_0$, the leading term has a temperature dependence.

For the investigated substances, the order parameter experimental data were fitted by a one-term equation with $\beta_0 \approx 0.355$. This means that the first correction term $B_2\tau^{\beta_2}$ in Eq. (7) equals zero and a region of symmetric behavior of the scaling function Eq. (12) must exist near the critical point for the liquid and vapor branches of the coexistence curve. The plots of $|\psi_{l,g}|$ vs $\tau^{\beta_1-\beta_0}$ will be linear and will converge symmetrically to the amplitude B_0. Such behavior is not observed for scaling functions for branches calculated, for example, for neon with the parameters $\beta_0 = 0.3272$, $T_c = 44.479$ K, and $\rho_c = 0.484$ g·cm^{-3} obtained in Ref. 7 and presented in Fig. 4a (curves 1 and 2) and for HD with parameters $\beta_0 = 0.325$,

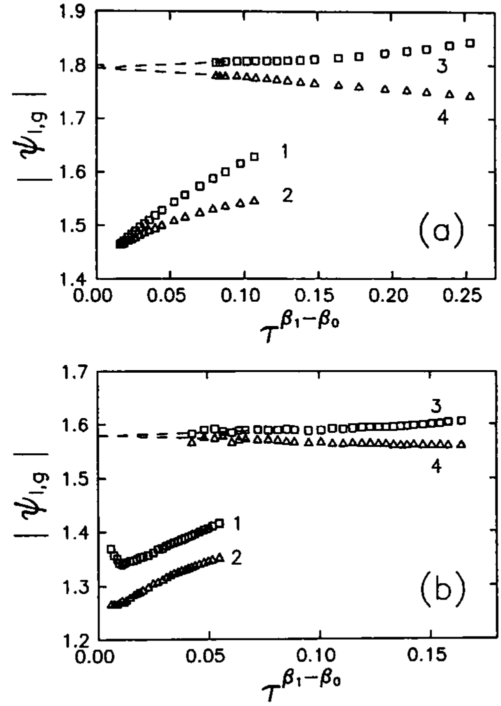

Fig. 4. Temperature dependences of scaling functions $|\psi_{l,g}|$ for the liquid (□) and vapor (△) branches, defined by Eq. (9) for Ne (a) and HD (b). For both fluids curves 1 and 2 are calculated with parameters β_0 and T_c obtained in Ref. 7, while curves 3 and 4 are calculated with β_0 and T_c, obtained in this paper.

$T_c = 35.957$ K, and $\rho_c = 0.0481$ g · cm^{-3} presented in Fig. 4b (curves 1 and 2). In both cases the value $\beta_1 = 0.89$ was used for the calculation of the value $\tau^{\beta_1 - \beta_0}$ (abscissa in Figs. 4a and b). The evident curvature toward lower values of B_0 indicates, in our opinion, an improper choice of the critical exponent values $\beta_0 = 0.3272$ (Ne), $\beta_0 = 0.325$ (HD), and the corresponding values of the critical temperature. This curvature means too that there is a temperature dependence of the leading term in Eq. (12). Naturally, when the critical parameters and critical indices for Ne and HD from Refs. 6 and 7 are used, one should expect neither symmetrical nor linear behavior of the coexistence curve branches.

Also, in Fig. 4a (curves 3 and 4) the scaling function $\psi_{l,g}$ for Ne with $T_c = 44.481$ K, $\beta_0 = 0.3575$, and $\beta_1 = 0.704$ obtained in this paper is shown. The intersection of liquid and vapor branches at $\tau = 0$ is observed for $\rho_c = 0.4836$ g · cm^{-3}, which differs from the value $\rho_c = 0.484$ g · cm^{-3} presented in Ref. 6 by the very small amount of 0.0004 g · cm^{-3}.

A similar analysis of the temperature dependence of the scaling functions was also carried out for HD (see Fig. 4b), N_2, and C_2H_4 and is evidence, in our opinion, that the asymptotic region is experimentally attainable for these substances.

With respect to the temperature dependence of the diameter, the experimental determination of the critical exponent β_1 is less accurate. Careful statistical analysis of experimental data for the HD diameter by Eq. (8) demonstrated enormous influence of the critical density value ρ_c on the magnitude of the exponent β_1 in Eq. (8) (see Ref. 5): a change in ρ_c by 1×10^{-5} g · cm^{-3} causes a change in β_1^{eff} from 0.75 to 0.90. Hence only simultaneous ρ_c and β_1 definition during the experimental data approximation by Eq. (8) with critical exponents and amplitudes as free parameters permits to obtain the best fit with $\beta_1 = 0.704 \pm 0.120 = 2\beta_0(\beta_0 = 0.352)$, $\beta_3 = 1.43 \pm 058 \approx 2\beta_1$. (The uncertainty assigned to β_1 does not include the uncertainty connected with the experimental error of the critical density.) Poor knowledge of the critical density may be a reason for the "specific" behavior of the HD coexistence curve diameter attributed to quantum effects [6].

3. CONCLUSIONS

In addition to the well-known poor convergence of the Wegner expansion, we point out that our analysis of these experimental data does not yield the Ising exponent value.

The fitting methods presented in this paper lead to the value of the critical exponent $\beta = \beta_0 = 0.355 \pm 0.003$ for a number of one-component fluids. A common value of $\beta = 0.355$, with slight adjustment of T_c, given a simpler and more accurate description of the coexistence curve than a Wegner expansion with Ising exponents.

In view of our results, we hope on further investigation of coexistence curve behavior near the liquid–gas critical point by means of both unprejudiced analysis of precise experimental data and theoretical efforts in this field.

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