

## PECULIARITIES OF THE LIQUID–GAS COEXISTENCE CURVE AND THE $\delta_T$ -CORRECTION NEAR THE CRITICAL POINT

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The results of our researches dealing with the peculiarities in the behavior of the liquid–gas coexistence curve on the diagram near to the critical point, which were carried out in the framework of the scaling theory with the use of the Clapeyron–Clausius equation, are reported. Making allowance for the asymmetry of the liquid–gas coexistence curve in the framework of the algebra of fluctuating variables enabled us to demonstrate that the derivative  $\left(\frac{dp}{dT}\right)_{cc}$  is finite at the critical point and to obtain a corresponding expression in terms of the critical parameters of the system. The theoretical results have been compared with experimental data for CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub>. The critical exponent for the temperature dependence of the Tolman  $\delta_T$ -correction has been calculated.

### 1. Introduction

Studies of the thermodynamic properties of substances in the vicinity of their liquid–vapor critical points are a challenging problem. While considering the features of the system behavior, the interaction between strongly developed fluctuations of the corresponding order parameter comes to the foreground as the critical point is approached, so that the details of intermolecular interaction become smoothed out. It is this circumstance that predetermines the universal behavior of systems of different nature near their critical points. Such a universality enables one, without specifying the substance, to obtain the important information concerning the singular behavior of a substance in the vicinity of its critical point. In this work, we are going to demonstrate that the derivative of the pressure with respect to the temperature calculated along the coexistence curve tends to a definite finite value as the system state approaches the critical one and to derive an expression for this derivative in terms of the critical parameters of the system. The result obtained will be applied to find the temperature behavior of the Tolman  $\delta_T$ -correction.

A necessary condition for the two phases of a one-component system to be in equilibrium is the equality of the chemical potentials  $\mu$  of their molecules. Therefore,

the equation

$$d\mu_l = d\mu_g, \quad (1.1)$$

where the subscripts  $l$  and  $g$  correspond to the liquid and vapor phases, respectively, determines the phase coexistence curve [1] in the differential form. Expressing the chemical potentials in terms of the pressure  $p$  and the temperature  $T$  in the system, we obtain the well-known Clapeyron–Clausius equation

$$\left(\frac{dp}{dT}\right)_{cc} = \frac{s_g^0 - s_l^0}{V_g^0 - V_l^0}, \quad (1.2)$$

where  $s^0$  and  $V^0$  are the entropy and the volume, respectively, per one particle, and the subscript  $cc$  corresponds to the coexistence curve. Hence, under declared conditions, the determination of the derivative is reduced to the elucidation of the behavior of the numerator and the denominator in formula (1.2) as the critical point is approached.

In the classical Landau theory of phase transitions, this quantity has indubitably no singularity. But if this theory is realized with engaging the van der Waals equation, then, while approaching the critical point,  $\left(\frac{dp}{dT}\right)_{cc} \rightarrow 4\frac{p_c}{T_c}$ , where  $p_c$  and  $T_c$  are the critical pressure and temperature, respectively. Really, by expanding the reduced van der Waals equation into a series in the vicinity of the critical point, we obtain the following expression:

$$\frac{p - p_c}{p_c} \approx -\frac{3}{2}\varphi^3 + 4\tau - 6\tau\varphi + 9\tau\varphi^2 - \frac{27}{2}\varphi^3\tau, \quad (1.3)$$

where  $\tau = \frac{T - T_c}{T_c}$  and  $\varphi = \frac{V - V_c}{V_c}$  are the relative deviations of the temperature and the volume, respectively, from their critical values  $T_c$  and  $V_c$ . In this case, like in the Landau theory, the shape of the coexistence curve in the vicinity of the critical point is governed by the power exponent  $\beta$ :  $\varphi \sim (-\tau)^\beta$ . In the van der Waals theory, the critical exponent of the coexistence curve is equal to 1/2.

By realizing the Landau theory with the help of the first or second Dieterici equation, we obtain that, in this limit,  $\left(\frac{dp}{dT}\right)_{cc} \rightarrow \frac{p_c}{T_c}$  or  $\left(\frac{dp}{dT}\right)_{cc} \rightarrow 5\frac{p_c}{T_c}$ , respectively.

## 2. Behavior of the Coexistence Curve in the Scaling Theory

According to the fluctuation theory of phase transitions [2], let us consider an arbitrary scalar quantity  $A_n(\mathbf{x})$  subjected to fluctuations, and the corresponding conjugated external field  $h_n(\mathbf{x})$ , where  $\mathbf{x}$  is the spatial variable. Those quantities are associated with an extra term in the fluctuation Hamiltonian  $\delta H_n = -\int h_n(\mathbf{x}) A_n(\mathbf{x}) d\mathbf{x}$  which was made dimensionless by its dividing by  $k_B T_c$ , where  $k_B$  is the Boltzmann constant. In so doing, the system is associated with a Hamiltonian which coincides with the corresponding thermodynamic potential. Such a Hamiltonian describes the behavior of the system in the sense that it provides correct average values for thermodynamic quantities, if a proper distribution function is made use of.

The expression for  $\delta H_n$  must remain invariant with respect to the scale transformations with an arbitrary scale factor  $\lambda$  [2],

$$A_n(\lambda x) \rightarrow \lambda^{-\Delta_n} A(x), \quad (2.1)$$

provided that the following scaling conditions are simultaneously imposed on the fields  $h_n$ :  $h_n \rightarrow \lambda^{-\Theta_n} h_n$ . It is evident that the sum of the corresponding scaling dimensionalities  $\Delta_n$  and  $\Theta_n$  must amount to the space dimension  $d$ .

According to the scaling theory [2], any scalar thermodynamic quantity which undergoes fluctuations in the given ensemble can be expanded in the basis of such quantities  $A_n(\mathbf{x})$  which are the eigenfunctions of the stretching operator with the scale dimensionality  $\Delta_n$  [see Eq. (2.1)].

Let  $A_1$  be a quantity with the smallest exponent  $\Delta_1$  in the algebra of fluctuating quantities in the liquid-vapor system, and let  $A_2$  be the next, by dimensionality ( $\Delta_2$ ), quantity in this algebra. Let us introduce the local dimensionless density of entropy  $\sigma(\mathbf{x})$  by using the expression

$$\frac{1}{V_c} \int \sigma(\mathbf{x}) d\mathbf{x} = - \left( \frac{\partial G}{\partial \tau} \right)_{P,N},$$

where  $G$  is the dimensionless thermodynamic Gibbs potential. Then, confining the consideration to two quantities which fluctuate most strongly, i.e. to the

relative volume and the entropy density, we write down the relations of the algebra of fluctuating quantities for relative deviations of the volume,  $\varphi = \frac{V-V_c}{V_c}$ , and the entropy density  $\bar{\sigma} = \sigma - \sigma_c$  from their critical values in the close vicinity of  $T_c$ :

$$\varphi = A_1 + bA_2, \quad \sigma = aA_1 + A_2. \quad (2.2)$$

It is known that the presence of second terms on the right-hand sides of expansions (2.2) means that the asymmetry of the coexistence curve is taken into account. The fields  $h_1$  and  $h_2$  conjugate to  $A_1(\mathbf{x})$  and  $A_2(\mathbf{x})$  are linear combinations of the quantities  $\tau = \frac{T-T_c}{T_c}$  and  $\pi = \frac{p-p_c}{p_c}$ :

$$h_1 = a\tau - \pi, \quad h_2 = \tau - b\pi, \quad (2.3)$$

they are also analogs of the parameter  $\tau$  and the magnetic field strength  $h$  for the ferromagnetic transition near the Curie point. Therefore, making use of the similarity relation, we obtain

$$\langle A_1 \rangle = h_2^\beta f(k), \quad \langle A_2 \rangle = h_2^{1-\alpha} g(k), \quad (2.4)$$

where  $k = h_1/h_2^{\beta+\gamma}$ ,  $f(k)$  and  $g(k)$  are some universal functions, and the broken brackets  $\langle \dots \rangle$  designate the averaging with a distribution function that is determined by the fluctuation Hamiltonian. In expressions (2.4), the standard notations were used for the critical exponents of the isochoric heat capacity ( $\alpha$ ), coexistence curve ( $\beta$ ), and isothermal compressibility ( $\gamma$ ).

In the vicinity of the critical point, the coexistence liquid-vapor curve is given – in terms of the  $(\pi, \tau)$ -variables – by the equation

$$h_1 = a\tau - \pi = 0, \quad \tau < 0. \quad (2.5)$$

It is evident that, in this case,  $h_2 = (1-ab)\tau$ . Then, making use of Eqs. (2.2) and (2.4), we obtain the equation of state which looks as

$$\frac{V-V_c}{V_c} = h_2^\beta f(k) + bh_2^{1-\alpha} g(k). \quad (2.6)$$

For the half-differences between the volumes and the entropies of the liquid and the vapor, we write down the following relations:

$$\frac{1}{2} (V_g - V_l) = V_c f(0) (1-ab)^\beta (-\tau)^\beta,$$

$$\frac{1}{2} (s_g - s_l) = \frac{1}{2} k_B (\sigma_g - \sigma_l) = k_B a f(0) (1-ab)^\beta (-\tau)^\beta. \quad (2.7)$$

It should be noted that the existence of the latent heat for the liquid–vapor transition,  $r_s = (s_g - s_l)T$ , testifies that the coefficient  $a$  in expansion (2.2) is different from zero.

By substituting the obtained relations (2.7) into the Clapeyron–Clausius equation, we obtain the required expression for the derivative,

$$\left(\frac{dp}{dT}\right)_{cc} = \frac{2af(0)(1-ab)^\beta(-\tau)^\beta k_B N}{2f(0)(1-ab)^\beta(-\tau)^\beta V_c N} = \frac{ak_B}{V_c}. \quad (2.8)$$

As was already mentioned, the dimensionless quantity  $a$  acquires a nonzero value; moreover, it is evident that  $a$  is not singular at the critical point, because all the scale dimensionality is included into the factor  $A_1$  in formula (2.2). Let us elucidate the sense of the constant  $a$  in formula (2.8). From Eq. (2.5) for the coexistence curve in the vicinity of the critical point, one can see that  $a$  satisfies the equation

$$ap_c V_c^0 = T_c \left(\frac{\mu - \mu_c}{T - T_c}\right)_{cc} + s_c^0 T_c, \quad (2.9)$$

where  $\mu = \mu_l(p, T) = \mu_g(p, T)$  is the common value for the chemical potentials of the liquid and vapor molecules along the coexistence curve of those two phases.

Hence, while approaching the critical point along the coexistence curve, we ultimately obtain

$$\begin{aligned} \left(\frac{dp}{dT}\right)_{cc} &= \frac{k_B T_c}{p_c (V_c^0)^2} \left( \left(\frac{\mu - \mu_c}{T - T_c}\right)_{cc} + s_c^0 \right) = \\ &= \frac{k_B T_c}{p_c (V_c^0)^2} \left( \lim_{T \rightarrow T_c} \left(\frac{d\mu}{dT}\right)_{cc} + s_c^0 \right). \end{aligned} \quad (2.10)$$

It should be emphasized that expression (2.10) could be derived directly, if one would consider an increment of the chemical potential in terms of the  $(p, T)$ -variables. Taking into account the behavior of the derivative  $\left(\frac{d\mu}{dT}\right)_{cc}$  when the critical point is approached, one may draw conclusion that the derivative  $\left(\frac{dp}{dT}\right)_{cc}$  acquires a finite nonzero value at the critical point itself.

We also note that the following relation between critical parameters can be derived from Eq. (2.10) for a certain group of substances which satisfy the law of corresponding states:

$$k_B \left(\frac{T_c}{P_c V_c^0}\right)^2 \left( s_c^0 + \lim_{T \rightarrow T_c} \left(\frac{d\mu}{dT}\right)_{cc} \right) = z, \quad (2.11)$$

where the number  $z$  is identical for all substances which obey the law of corresponding states and can

be determined from the reduced equation of state. It is evident that  $z$  is equal to the value of the reduced pressure derivative with respect to the reduced temperature at the critical point.

### 3. Comparison of Theoretical Results with Experimental Data

The experimental data for the dependence of the latent heat of the liquid–vapor transition on the temperature were taken from work [3]; they are exhibited in the figure on the logarithmic scale. The table contains the slope coefficients for the straight lines drawn through seven, three, or two points which are nearest to the critical one. As the approximation interval converges to the critical point, the calculated value of the exponent  $\beta$  tends expectedly to the corresponding value known from the literature [4].

According to the experimental data obtained in work [4], for the deviation of the density  $\Delta\rho = \rho - \rho_c$  which is approximated by the formula  $\Delta\rho = \pm B_0(-\tau)^{\beta_0} + B_1(-\tau)^{\beta_1}$ , the following values of the critical indices  $\beta_0$  and  $\beta_1$  in the temperature interval  $\tau \approx 10^{-4} \div 10^{-3}$  were obtained: for  $C_2H_6$ ,  $\beta_0 = 0.338 \pm 0.006$  and  $\beta_1 = 0.90 \pm 0.05$ ; for  $CO_2$ ,  $\beta_0 = 0.347 \pm 0.006$  and  $\beta_1 = 0.90 \pm 0.05$ ; and, for  $Xe$ ,  $\beta_0 = 0.340 \pm 0.003$  and  $\beta_1 = 0.77 \pm 0.13$ . One can see that, within the error limits, the agreement is observed between the theory and the experiment.

### 4. Determination of the Temperature Behavior of the Tolman $\delta_T$ -Correction Near the Critical Point for a Spherical Droplet

Let us apply the results obtained and determine the temperature behavior of the so-called Tolman  $\delta$ -correction in the vicinity of the critical point. As is known, the dependence of the surface tension coefficient of a spherical droplet on its radius is described by the Gibbs–Tolman–König–Buff equation [5]

$$\ln \frac{\sigma(R)}{\sigma_\infty} = \int_\infty^R dr \frac{\frac{2\sigma}{r^2} \left\{ 1 + \frac{\delta_T}{r} + \frac{1}{3} \left(\frac{\delta_T}{r}\right)^2 \right\}}{1 + \frac{2\delta_T}{r} \left\{ 1 + \frac{\delta_T}{r} + \frac{1}{3} \left(\frac{\delta_T}{r}\right)^2 \right\}}, \quad (4.1)$$

The values of the critical exponent  $\beta$  for the latent heat of the liquid–vapor transition calculated with the use of seven, three, or two experimental points

Substance	$\beta$ {7}	$\beta$ {3}	$\beta$ {2}
$CO_2$	$0.373 \pm 0.08$	$0.350 \pm 0.011$	$0.339 \pm 0.05$
$C_2H_6$	$0.369 \pm 0.05$	$0.362 \pm 0.05$	$0.353 \pm 0.06$

where  $\sigma_\infty$  is the surface tension coefficient for the plane interface, and  $\delta_T$  is a correction introduced by Tolman [6]. Provided that  $\delta_T$  is a constant, integral (4.1) can be calculated analytically [7], and, if  $\frac{\delta_T}{R} \ll 1$ , the dependence  $\sigma = \sigma(R)$  can be written down – in the first approximation in the small parameter  $\frac{\delta_T}{R}$  – in the form which looks like the well-known Tolman formula [5]

$$\sigma = \sigma_\infty \left( 1 - \frac{2\delta_T}{R} \right). \quad (4.2)$$

If one takes the isothermal equation of state for a liquid in the form  $p - p_0 = f\left(\frac{V_0 - V}{V_0}\right)$ , where  $f$  is a definite function, and  $V_0$  is a point on the coexistence curve, the Tolman  $\delta$ -correction in a wide temperature interval is determined, as was demonstrated in works [8, 9], by the expression

$$\delta_T = \frac{4f'(0) - 3f''(0)}{6(f'(0))^2} \sigma_\infty, \quad (4.3)$$

where the derivatives are calculated at a coexistence curve point, provided a constant temperature. Equation (4.3) can be rewritten in terms of the isothermal compressibility  $\beta_T$  as follows:

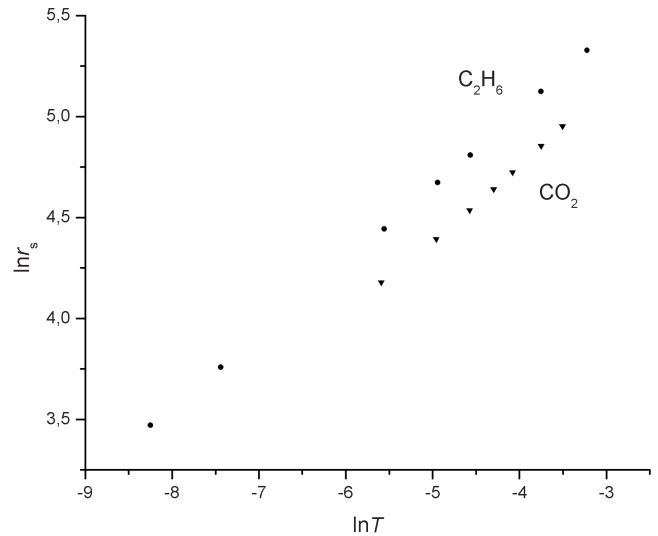
$$\delta_T = \left[ \frac{1}{6} \beta_T + \frac{1}{2\beta_T} \left( \frac{\partial \beta_T}{\partial p} \right)_T \right] \sigma_\infty. \quad (4.4)$$

Let us determine which of summands in formula (4.4) dominates near the critical point. For this purpose, let us express the isothermal compressibility as a function of  $(V, p)$  or  $(V, T)$  and write down its isothermal derivative with respect to the pressure:

$$\left( \frac{\partial \beta_T}{\partial p} \right)_T = \left( \frac{\partial \beta_T}{\partial T} \right)_V \left( \frac{\partial T}{\partial p} \right)_V + \left( \frac{\partial \beta_T}{\partial V} \right)_p \left( \frac{\partial V}{\partial p} \right)_T. \quad (4.5)$$

According to the scaling theory, the derivative of the pressure with respect to the temperature at the critical point on the coexistence curve (as well as on the isochore) is finite. Therefore, we obtain that the addend and the addend are the quantities of the order of  $(-\tau)^{-\gamma-1}$  and  $(-\tau)^{-2\gamma-\beta}$ , respectively, near the critical point. Hence, the addend on the right-hand side of Eq. (4.5) dominates there. Then, the addend and the addend in the brackets on the right-hand side of formula (4.4) are of the order of  $(-\tau)^{-\gamma}$  and  $(-\tau)^{-\beta\delta}$ , respectively. Making use of the known relation  $-\gamma = -\beta(\delta - 1)$  between the critical exponents, we obtain that the Tolman correction reads

$$\delta_T \sim (-\tau)^{-\gamma-\beta} \sigma_\infty = (-\tau)^{-\beta\delta} \sigma_\infty. \quad (4.6)$$



Measurement data of the temperature dependence of the latent heat of the liquid-vapor transition for CO<sub>2</sub> and C<sub>2</sub>H<sub>6</sub> [3]

Taking into account that the surface tension coefficient tends to zero at the critical point following the law  $\sigma_\infty \sim (-\tau)^{(d-1)\nu} \sim (-\tau)^{2-\alpha-\nu} = (-\tau)^{\gamma+2\beta-\nu}$ , where  $\nu$  is the critical exponent for the correlation length, a corresponding scaling relation can be written down for the Tolman  $\delta_T$ -correction in a three-dimensional space as

$$\delta_T \sim (-\tau)^{\gamma+2\beta-\nu-\gamma-\beta} = (-\tau)^{-(\nu-\beta)}, \quad (4.7)$$

where the power exponent  $\nu - \beta$  is approximately equal to 0.32.

Thus, since  $\nu - \beta > 0$ , the Tolman  $\delta_T$ -correction is singular at the critical point, which is confirmed by the results of experiments [10]. Therefore, it must be taken into account in the vicinity of the critical point. We note that the singular behavior of the surface tension coefficient can be associated with “non-smoothness” of the droplet surface, which is responsible for the formation of clusters of the “seaweed-like” type with a fractal dimensionality of the surface, rather than compact three-dimensional spherical aggregates [11].

## 5. Conclusions

It has been demonstrated that the account of the asymmetry of the liquid-vapor coexistence curve in the framework of scaling theory allows one to adequately

describe the behavior of this curve in the vicinity of the critical point. An expression for the pressure derivative with respect to the temperature on the coexistence curve at  $T \rightarrow T_c$  has been deduced, and the value of this expression has been found finite and nonzero.

A relation between critical parameters, which is a reflection of the law of corresponding states, has been obtained.

The finiteness of the specified derivative was used to find the critical exponent for a singular temperature behavior of the Tolman  $\delta_T$ -correction, which amounts to  $\beta - \nu \approx -0.32$ .

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#### ОСОБЛИВОСТІ ПОВЕДІНКИ КРИВОЇ СПІВІСНУВАННЯ РІДИНА-ПАРА ТА $\delta_T$ -ПОПРАВКИ ПОВБЛИЗУ КРИТИЧНОЇ ТОЧКИ

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#### Резюме

Наведено результати дослідження особливостей поведінки кривої співіснування рідина-пара на  $p - T$ -діаграмі поблизу критичної точки, проведено на основі теорії скейлінгу з використанням рівняння Клапейрона-Клаузіуса. Врахування в рамках алгебри величин, що зазнають флуктуацій, асиметрії кривої співіснування рідина-пара дозволило показати, що похідна  $\frac{dp}{dT}$  в критичній точці є скінченною, та отримати вираз для неї через критичні параметри системи. Результати порівняно з експериментальними даними для  $\text{CO}_2$  і  $\text{C}_2\text{H}_6$ . Знайдено критичний показник для температурної поведінки  $\delta_T$ -поправки Толмена.