

SINGULARITY OF BINODAL DIAMETER IN ENTROPY–TEMPERATURE TERMS FOR ATOMIC AND MOLECULAR LIQUIDS

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The behavior of a binodal diameter for atomic and molecular liquids has been studied in the entropy–temperature terms in a vicinity of the critical point. By extracting the regular part in the temperature dependence of the binodal diameter, the existence of the $|\tau|^{2\beta}$ -anomaly has been revealed.

1. Introduction

The asymmetry of the phase coexistence curve is a characteristic feature of real systems, in which the particle–hole symmetry is broken. Such a symmetry is inherent in lattice models of the Ising type, because the excluded volume effects, which are associated with own particle dimensions, are absent here. An equal-weighted sum of values for any physical quantity that distinguishes between coexisting phase states can be taken for the parameter of such an asymmetry. For coexisting liquid and vapor, we have

$$\varphi_d = \frac{\varphi_l + \varphi_g}{2}. \quad (1)$$

where the difference $\varphi_l - \varphi_g$ is no more than the order parameter for the system concerned. It is evident that, in the absence of particle–hole symmetry, an adequate primitive quantity can be either the density or the number of particles per unit volume. It is the diameter of the density–temperature coexistence curve that satisfies the classical law of rectilinear diameter [1],

$$n_d = \frac{\tilde{n}_l + \tilde{n}_g}{2} = 1 + A\tau, \quad \tau = \frac{T - T_c}{T_c} < 0, \quad (2)$$

where $\tilde{n}_i = n_i/n_c$ ($i = l, g$), and n_l and n_g are the densities of the liquid and gas phases, respectively, which are normalized to the critical density n_c . Note that this law is approximate; however, it is valid practically in the whole temperature interval from the ternary critical

point, except for a vicinity of the critical point, where abnormal density fluctuations leads to the appearance of nonanalytic contributions to Eq. (2) [2]. These contributions are governed by the corresponding contributions to the Hamiltonian of the system that violate the Ising symmetry of the Hamiltonian with respect to the transformation ($h \rightarrow -h, \varphi \rightarrow -\varphi$), where h is the field conjugate to the order parameter φ . The issue on the singularity structure for the order parameter diameter has a long history, but recently this problem became challenging again owing to the works by M. Fisher and other authors [3–6].

For a long time, the asymptotics of the coexistence curve diameter was believed to have the following structure:

$$n_d = D_{1-\alpha} |\tau|^{1-\alpha} + D_1 |\tau| + \dots \quad (3)$$

Therefore, experimental data were also approximated by expression (3) to reveal just that singularity [7–9]. The renormalization group analysis confirmed the singular behavior of the binodal diameter 3 and connected it with the presence of odd-order terms $\varphi(\nabla\varphi)^2\varphi^5$ in the Hamiltonian [10]. In work [10], it was demonstrated that, besides the well-known $(1 - \alpha)$ -singularity, there exists another one. At the same time, the corresponding index was not calculated in the explicit form owing to a bad convergence of the ε -expansion. It is also worth noting that earlier, in works [2, 11], it was shown that the singularity of the coexistence curve diameter can be stronger than that in expression (3), namely,

$$n_d = D_{2\beta} |\tau|^{2\beta} + D_{1-\alpha} |\tau|^{1-\alpha} + D_1 |\tau| + \dots \quad (4)$$

The characteristic values of the amplitudes $D_{1-\alpha}$ and $D_{2\beta}$, as well as their dependences on the parameters of the particle-to-particle interaction, have been discussed till now [12, 13]. In work [14] on the basis of the canonical approach [15], it was shown that the signs of amplitudes

in the first and second terms of expression (4) are opposite. In terms of the canonical variables, their ratio is universal. This result corresponds to the results obtained when approximating experimental data [16]. It is this feature that brings about rather an insignificant singularity value for the coexistence curve diameter in the density–temperature terms for the majority of molecular liquids. It was this circumstance that did not allow the problem concerning the presence of a more singular contribution $|\tau|^{2\beta}$ in Eq. (4) to be unambiguously solved earlier. It is clear that, depending on the amplitude in Eq. (4), the singularity can be weakly pronounced, if the terms with different signs compensate each other. Therefore, an *a priori* estimate of amplitudes is important from the viewpoint of the procedure validity for a treatment of experimental data. Moreover, the amplitudes of singular contributions depend on the choice of an order parameter.

This work aimed at studying the structure of the coexistence-curve-diameter singularity in terms of the density and the entropy as the most natural order parameters for liquid–vapor transitions. On the basis of the canonical approach [14], we demonstrated that, by extracting regular contributions which can be determined by analyzing the behavior in the region far from the critical point, the presence of the contribution $|\tau|^{2\beta}$ to the singularity behavior of the coexistence curve diameter becomes evident owing to different amplitude signs in the corresponding singular contributions.

2. Binodal Asymmetry and Diameter Singularity in the Framework of the Canonical Approach

According to the results of work [2], the emergence of a more singular contribution with the index of 2β is associated with the total $P - \mu - T$ symmetry of the scaling equation of state

$$\Phi = |A_2|^{2-\alpha} f_s \left(\frac{A_1}{A_2^{\beta+\gamma}} \right) + \dots, \quad (5)$$

where the fields Φ , A_1 , and A_2 are functions of the physical pressure, P , chemical potential, μ , and temperature, T , fields. This form of the equation of state arises naturally within the approach based on the canonical form of the fluctuation Hamiltonian [14, 15, 17]. The essence of this approach consists in the following. The effects of a coexistence curve asymmetry are directly coupled with an asymmetry of the microscopic Hamiltonian which is regarded as a density functional. Really, the descrip-

tion of the equations of state for a liquid in terms of the molecular density in the presence of effects of the own molecular volume violates the particle–hole symmetry that is characteristic of the Ising model. Bearing the catastrophe theory [18] in mind, the nonsymmetric terms can be eliminated from the Hamiltonian by carrying out a nonlinear transformation of the order parameter field,

$$\varphi(\mathbf{r}) = \eta(\mathbf{r}) - \frac{1}{2} \Gamma_2 \eta(\mathbf{r})^2 + \dots \quad (6)$$

Here, $\varphi(\mathbf{r})$ is the laboratory order parameter, e.g., the density; and $\eta(\mathbf{r})$ is the canonical order parameter, in terms of which the Hamiltonian has the form of Ginzburg–Landau functional,

$$\mathcal{H}_{LG}[\eta(\mathbf{r})] = \int \left(A_1 \eta(\mathbf{r}) + \frac{A_2}{2} \eta^2(\mathbf{r}) + \frac{A_4}{4} \eta^4(\mathbf{r}) + \frac{1}{2} (\nabla \eta(\mathbf{r}))^2 \right) dV. \quad (7)$$

According to the results of work [19], the average value of the canonical order parameter, $\langle \eta \rangle$, is

$$\langle \eta \rangle = - \left. \frac{\partial \Phi}{\partial A_1} \right|_{A_1=0} = \pm |\tilde{\tau}|^\beta g_s(0) + \dots, \quad (8)$$

$$\tilde{\tau} = A_2|_{A_1=0} = a t + o(t),$$

where $g_s(x) = f'_s(x)$. The function $f_s(x)$ satisfies the symmetry condition $f_s(x) = f_s(-x)$ which is equivalent to the reconstruction of the equation-of-state symmetry.

Since η is a symmetric order parameter, the rectilinear binodal diameter $\varphi^{(d)}$ can be written in terms of the canonical order parameter as follows [14]:

$$\varphi^{(d)} = -\frac{1}{2} \tilde{\Gamma}_2 [g_s^2(0) |\tilde{\tau}|^{2\beta} + l_s(0) |\tilde{\tau}|^{1-\alpha}] + \dots \quad (9)$$

Here, $\tilde{\Gamma}_2$ is defined as

$$\tilde{\Gamma}_2 = \Gamma_2|_{A_1=0}. \quad (10)$$

In real experiments, the actual temperature variable τ rather than the canonical temperature $\tilde{\tau}$ is observed. Therefore, for the experimental analysis of the diameter singularity, we obtain

$$\varphi^{(d)} = -\frac{1}{2} \tilde{\Gamma}_2 [g_s^2(0) a^{2\beta} |\tau|^{2\beta} + l_s(0) a^{1-\alpha} |\tau|^{1-\alpha}] + \dots \quad (11)$$

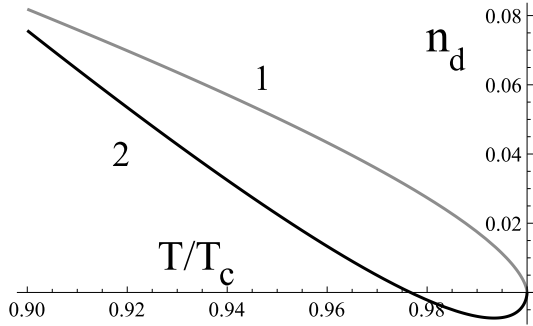


Fig. 1. Probable scenarios for the temperature behavior of the coexistence curve diameter in terms of the density–temperature: (1) $-D_1 \approx D_{1-\alpha} < 0$ and $D_{2\beta} > 0$, and (2) $D_1 \approx D_{1-\alpha} > 0$ and $D_{2\beta} < 0$

Hence, the amplitudes D_i which are determined by approximating experimental data with the help of formula (4) read as follows:

$$D_{1-\alpha} = -\frac{1}{2} \tilde{\Gamma}_2 a^{1-\alpha} l_s(0), \quad D_{2\beta} = -\frac{1}{2} \tilde{\Gamma}_2 a^{2\beta} g_s^2(0). \quad (12)$$

They are different from zero simultaneously, if $\tilde{\Gamma}_2 \neq 0$. Moreover, since $l_s(0) < 0$, the indicated amplitudes have opposite signs, and their ratio,

$$\frac{D_{2\beta}}{D_{1-\alpha}} = a^{2\beta+\alpha-1} \frac{g_s^2(0)}{l_s(0)} < 0, \quad (13)$$

weakly depends on the substance type which is defined by the coefficient a . Therefore, singular contributions to the coexistence curve diameter in the density–temperature terms have the same origin, so they have to be considered simultaneously. The parameter Γ_2 is determined by the asymmetric part of the microscopic Hamiltonian, and it can be associated with characteristics of the particle-to-particle interaction [14].

It should be noted that it is the fluctuation nature of the coexistence curve diameter singularity in the density–temperature terms that is responsible for the sign anticorrelation between the amplitudes $D_{1-\alpha}$ and $D_{2\beta}$, as well as for the approximate invariance of their ratio. Note that, within the mean-field approximation, the analysis of many equations of state, which was carried out in work [13] in the framework of the approach proposed in works [4, 6, 20], also revealed such sign anticorrelation. However, in such an approach, the authors did not consider the amplitudes D_i ($i = 2\beta, 1-\alpha$), but their mean-field analogs which form the coefficient of the classical linear contribution, $\sim |\tau|$, to the density diameter. Such an approach is based on the fact that, in the mean-field approximation, the contributions $\sim |\tau|^{2\beta}$ and

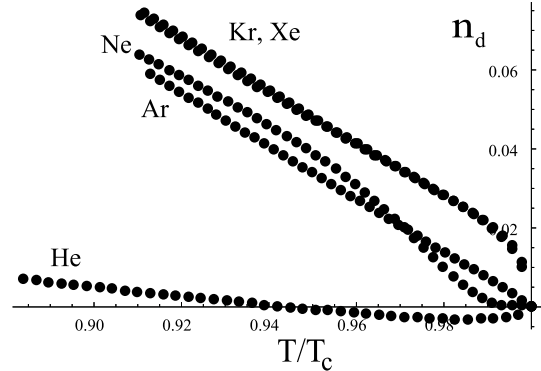


Fig. 2. Temperature dependences of the coexistence curve diameter in the density–temperature terms for various noble gases according to the data of work [22]

$\sim |\tau|^{1-\alpha}$ become degenerate into the linear dependences. As was marked by the authors of work [13], there are no *a priori* relations between the mean-field quantities determined in such a way and the actual fluctuation ones. Therefore, in work [13], the ratio between the indicated amplitudes does not manifest any regularity similar to that found above.

3. Probable Scenarios of the Temperature Behavior of the Diameter

The temperature behavior of the density diameter coexistence curve (4) depends considerably on the ratio between the amplitudes D_i of corresponding contributions. It is evident that $D_1 > 0$. Moreover, the slope of the classical law for the rectilinear diameter is determined by the critical and Boyle temperatures [21]. Since the $|\tau|^{2\beta}$ -singularity is the strongest one, the nonmonotonous behavior of diameter in the fluctuation region takes place, if $D_\alpha > 0$ and $D_{2\beta} < 0$. For such a behavior to manifest itself exactly, the amplitudes of singular contributions have to satisfy the condition $|D_{1-\alpha}/D_{2\beta}| \lesssim 1$ (see Fig. 1). However, if $D_{2\beta} > 0$, this singularity can be obscured by other two contributions, provided that $D_{1-\alpha} < 0$ and $D_1 \approx |D_{1-\alpha}|$, if $|D_{2\beta}/D_{1-\alpha}| \ll 1$. Therefore, the issue concerning the calculation of the order parameter diameter amplitudes is important from the viewpoint of the correct treatment of experimental data.

4. Extraction Procedure for the Regular Part of the Diameter

It is clear that the cases $D_{2\beta} > 0$ and $D_{2\beta} < 0$ must correspond to different physical situations. This can be evidently seen while comparing the coexistence curve

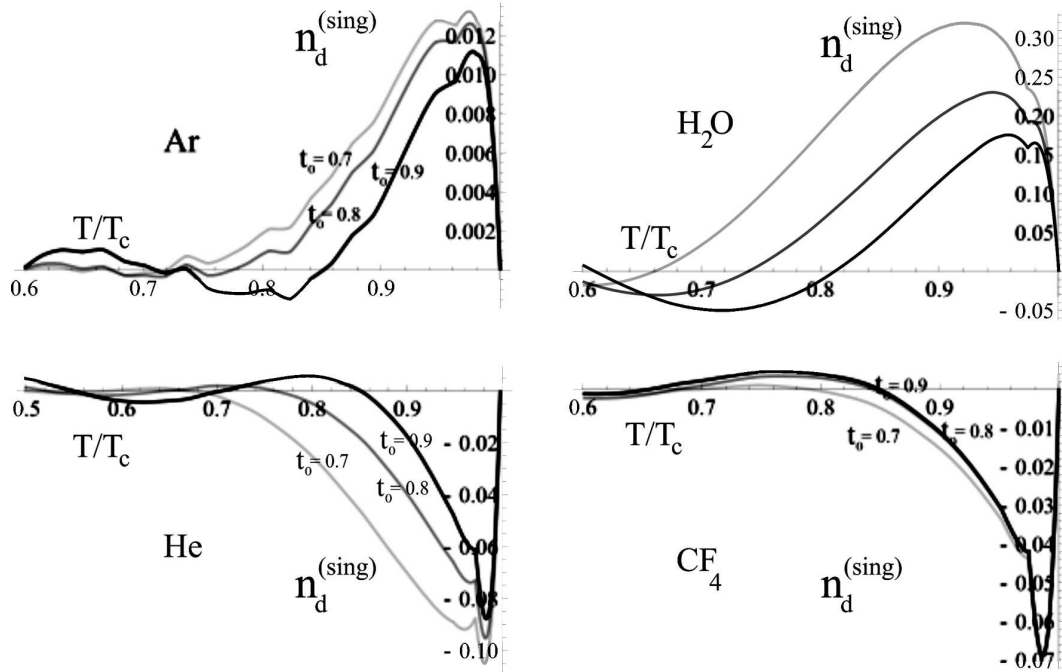


Fig. 3. Temperature dependences $n_d^{(\text{sing})}(t, t_0)$ for some atomic and molecular liquids and various t_0

diameters for such liquids as helium and neon, on the one hand, and argon, krypton, and xenon, on the other hand (see Fig. 2). The figure demonstrates that, for light quantum liquids of the helium (He) and neon (Ne) types, the case $D_{2\beta} < 0$ takes place. For heavy (classical) Ar, Kr, and Xe liquids, we have $D_{2\beta} > 0$. It is also clear that the values of amplitudes $D_{2\beta}$ and $D_{1-\alpha}$ are the same for the liquids that belong to the same class of universality. As was shown in work [14], the amplitudes $D_{2\beta}$ and $D_{1-\alpha}$ must possess different signs. Therefore, the fluctuation part of the diameter has a nonmonotonous temperature dependence. In order to extract the fluctuation part from n_d , we have to separate the regular contribution

$$n_d^{(\text{sing})} = n_d - n_d^{(\text{reg})},$$

where the regular part

$$n_d^{(\text{reg})}(t, t_0) = \sum_{k=1}^N a_k(t_0) (1-t)^k$$

can be determined from the behavior of the diameter n_d in the temperature interval $t < t_0 < 1$ located far from the critical point ($0.7 \leq t_0 \leq 0.9$). As we approach the fluctuation region, the deviations from the regular dependence grow owing to fluctuation effects. The results of such deviations are illustrated in Fig. 3. The singular

part affects the regular behavior only in the fluctuation region. It is clear that the dependences $n_d^{(\text{sing})}$ presented in Figs. 3, a and b correspond to the case $D_{2\beta} > 0$ and $D_{1-\alpha} < 0$ (scenario 1). At the same time, the behavior presented in Figs. 3, c and d take place, if $D_{2\beta} < 0$ and $D_{1-\alpha} > 0$ (scenario 2).

After the quantity $n_d^{(\text{sing})}(t, t_0)$ had been determined at a given t_0 , the data were treated with the use of formula (4), in which the critical indices $\alpha = 0.11$ and $\beta = 1/3$ were selected to be fixed, and the coefficients D_i ($i = 1, 1-\alpha, 2\beta$) served as fitting parameters. The ratio $D_{2\beta}/D_{1-\alpha}$ is a function of the fluctuation interval $0.07 < 1-t_0 < 0.3$, which corresponds to characteristic values of the Ginzburg parameter for molecular liquids. The results obtained (see Fig. 4) testify that this ratio does depend weakly on the sort of a liquid.

To confirm this assertion, we present the results of calculations of the ratio $D_{2\beta}/D_{1-\alpha}$ for ion-electronic liquids of Cs and Rb, for which the binodal asymmetry is higher than that in the case of molecular liquids. The singularity structure of the coexistence curve diameter for those systems was studied in works [23]. In particular, the comparative analysis of the results obtained at the treatment of data with the help of expressions (3) and (4) gave rise to a conclusion that $|D_{2\beta}/D_{1-\alpha}| \lesssim 1/30$ [23]. However, the circumstance that the data of work [23] cover rather a wide temperature interval $10^{-3} \lesssim |\tau| \lesssim 10^{-1}$

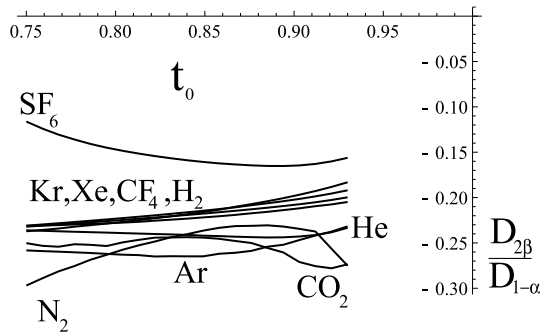


Fig. 4. Dependences of the amplitude ratio $D_{2\beta}/D_{1-\alpha}$ on the parameter t_0 for some atomic and molecular liquids

forced us to take the contribution of the regular part $n_d^{(\text{reg})}$ into consideration. The procedure of extraction of the diameter regular-part considerably changes this result, which amounts to $D_{2\beta}/D_{1-\alpha} \approx -0.34$ (see Fig. 5) and correlates with the result obtained above for atomic and molecular liquids.

The result obtained also agrees well with the conclusion that, despite the different nature of microscopic interactions in liquid metals and molecular liquids, those two types of substances demonstrate the same thermodynamic behavior in the critical region “liquid–vapor” and belong to the same class of generalized thermodynamic similarity [24]. This circumstance follows from the short-range character of the effective ion-to-ion interaction and allows alkaline metals to be considered in the framework of the global isomorphism with a lattice gas (the Ising model) [21, 25]. In particular, it gives the explanation to the fact that the binodal of alkaline metals, as well as that of atomic and molecular liquids with a short-range interaction between particles, can be described well in the zeroth-order approximation by the global cubic law [26]

$$n_{\text{liq}} - n_{\text{gas}} = B_0 |\tau|^\beta, \quad \beta \approx 0.33.$$

5. Binodal Diameter in Entropy–Temperature Terms

Let us determine the coexistence curve diameter in terms of the entropy–temperature in a way similar to Eq. (1):

$$S_d = \frac{S_l + S_g}{2} - S_c, \quad (14)$$

where $S_{l,g}$ are the entropies of the coexisting liquid and gas phases, respectively; and S_c is the entropy value at the critical point. As was shown in work [27], the quantity S_d is more informative for the characterization of a

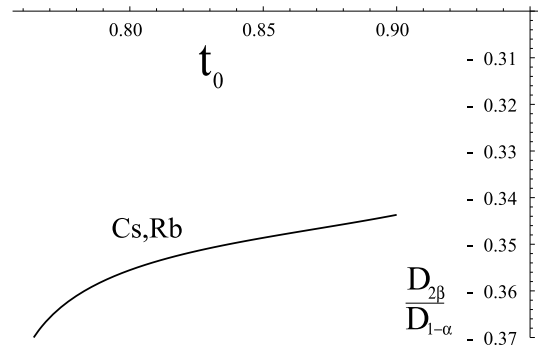


Fig. 5. Dependence of the amplitude ratio $D_{2\beta}/D_{1-\alpha}$ on the parameter t_0 for Cs and Rb

phase equilibrium asymmetry than the coexistence curve diameter in terms of the density–temperature. Really, in contrast to the density case, the temperature dependence of S_d along the binodal is nonmonotonous and depends considerably on the number of molecular degrees of freedom and the character of a molecular rotational motion in the liquid phase, because the entropy itself looks like

$$S = S_c + S^{(\text{id})} + S^{(\text{ex})}. \quad (15)$$

Here,

$$S^{(\text{id})} = c_v^{(\text{id})} \ln \frac{T}{T_c} - \ln \frac{n}{n_c} \quad (16)$$

is the entropy contribution that corresponds to the ideal gas, $c_v^{(\text{id})} = \frac{k}{2}$, k is the number of molecular degrees of freedom, and

$$S^{(\text{ex})} = c_v^{(\text{ex})} \ln \frac{T}{T_c} + f(n) \quad (17)$$

is an excess part of the entropy. The character of a nonmonotonous behavior of the diameter is governed by a competition between the contributions made by the ideal-gas and excess entropies. The latter is related to correlation effects of the particle-to-particle interaction. The general behavior of S_d for molecular and atomic liquids was analyzed by us in work [27]. Below, we will analyze the behavior of S_d in the fluctuation region. A more informative content of the diameter in the entropy–temperature terms follows from the fact that the singular behavior of the diameter in terms of the density is known to be related to energy fluctuations and, as a consequence, to the singularity of the specific heat c_v [19]. Since it is just the entropy that is directly connected with the heat capacity, the analysis of the binodal diameter in the entropy–temperature terms allows an extra 2β -singularity to be extracted, besides the known $(1 - \alpha)$ -singularity associated with the heat capacity contribution.

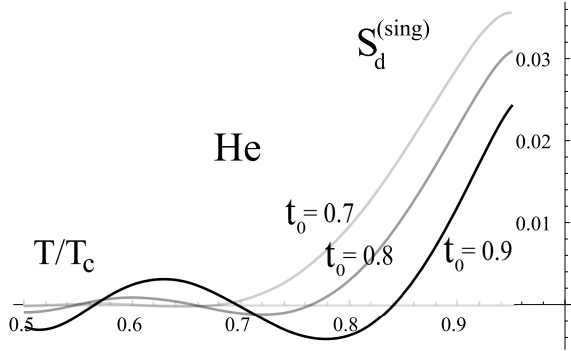


Fig. 6. Temperature behavior $S_d^{(\text{sing})}(t, t_0)$ for He at various t_0

First, let us analyze the behavior of S_d in the framework of the mean-field approximation. In this approximation, we have

$$\delta\tilde{n}_{l,g} = \pm b\sqrt{|\tau|} + a|\tau| + \dots \quad (18)$$

for the density. Expanding S_d at the critical point in a series in a small density deviation and using Eq. (15), we obtain

$$S_d = n_c \left. \frac{\partial S}{\partial n} \right|_c n_d + \frac{c_v^{(l)} + c_v^{(g)}}{2} \ln \frac{T}{T_c} + \frac{1}{4} \left. \frac{\partial^2 S}{\partial n^2} \right|_c (\delta n_l^2 + \delta n_g^2) + \dots \quad (19)$$

Taking the thermodynamic relations

$$\left. \frac{\partial S}{\partial n} \right|_c = - \frac{1}{n_c} \left. \frac{\partial p}{\partial T} \right|_c < 0, \quad (20)$$

$$\frac{\partial^2 S}{\partial n^2} = \frac{2}{n^3} \frac{\partial p}{\partial T} - \frac{1}{n^2} \frac{\partial^2 p}{\partial T \partial n} \quad (21)$$

into account and neglecting the terms with higher powers of the temperature, we arrive at the expression

$$S_d = - \left[\frac{1}{n_c} \left. \frac{\partial p}{\partial T} \right|_c (a - b^2) + b^2 \frac{\partial^2 p}{\partial n \partial T} + \frac{c_v^{(l)} + c_v^{(g)}}{2} \right] |\tau| + o(|\tau|). \quad (22)$$

The coefficients a and b are determined by the equation of state for the substance. In particular, for the van der Waals equation, $a = 2/5$, $b = 2$, and $dS_d/d\tilde{T} = 0.6$; for the Berthelot equation, $a = 2/5$, $b = 2\sqrt{2}$, and $dS_d/d\tilde{T} = 1.35$.

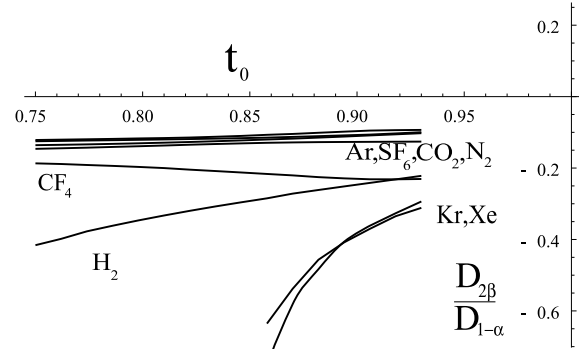


Fig. 7. Amplitude ratios $D_{2\beta}/D_{1-\alpha}$ determined from the analysis of the singular part of the diameter in terms of the entropy-temperature for some atomic and molecular liquids

In the fluctuation region, the singularity of S_d is governed by the corresponding singular contributions of the heat capacity and the density. Since $\left. \frac{\partial^2 p}{\partial n \partial T} \right|_c = 0$, Eq. (22) reads

$$S_d = S_{2\beta} |\tau|^{2\beta} + S_{1-\alpha} |\tau|^{1-\alpha} + \dots, \quad (23)$$

where

$$S_{2\beta} = \frac{1}{n_c} \left. \frac{\partial p}{\partial T} \right|_c (B_\beta^2 - D_{2\beta}), \quad (24)$$

$$S_{1-\alpha} = -A - D_{1-\alpha} \frac{1}{n_c} \left. \frac{\partial p}{\partial T} \right|_c.$$

The coefficients $A > 0$ and $B_\beta > 0$ are the critical amplitudes of the heat capacity and the density, respectively:

$$c_v = A |\tau|^{-\alpha} + \dots, \quad \delta\tilde{n}_{l,g} = \pm B_\beta |\tau|^\beta + \dots$$

It should be noted that, in contrast to the density case, the coefficient $S_{1-\alpha}$ for the coexistence curve diameter in terms of the entropy-temperature contains a contribution that is not connected with the Hamiltonian asymmetry, but stems exclusively from the heat capacity singularity. From the general analysis of the coexistence curve diameter in terms of the density-temperature presented in the previous section, it follows that $|D_{2\beta}/D_{1-\alpha}| \approx 0.15 \div 0.2$ (see also work [16]). Therefore, one should expect that $S_{2\beta} > 0$ and $S_{1-\alpha} < 0$, so that the singular part of the diameter in terms of the entropy-temperature would behave similarly to what is depicted in Figs. 3, *a* and *b*, even if $|D_{2\beta}| > |D_{1-\alpha}|$. This is really the case (see Fig. 6).

To single out the contribution made by the density singularity only, it is necessary to analyze the quantity

$$\tilde{S} = S - c_v \ln \frac{T}{T_c} + \ln \frac{n}{n_c}.$$

The results of calculations of the amplitude ratio with the use of the entropy data and formulas (23) and (24) are exhibited in Fig. 7. The figure evidences that the obtained values fall within the interval $|D_{2\beta}/D_{1-\alpha}| \approx 0.1 \div 0.2$, which agrees with the results of the analysis of data for the coexistence curve diameter in terms of the density–temperature which were presented in Sec. 2. Thus, the obtained results testify to the singular $|\tau|^{2\beta}$ -behavior of the order parameter diameter and correlate with theoretical conclusions about the amplitudes of corresponding singular contributions.

6. Conclusion

The singularity structure of the coexistence curve diameter in terms of the density–temperature and entropy–temperature has been considered. By extracting the regular contributions which can be determined from the behavior of the diameter in the thermodynamic region, where fluctuation contributions are absent, the singular contribution $\sim |\tau|^{2\beta}$ was revealed. In the framework of the canonical formalism, it is shown that the ratio between the amplitudes for singular contributions is universal in terms of the temperature variable conjugate to the canonical order parameter. This theoretical conclusion agrees well with that obtained while analyzing experimental data on the density, entropy, and coexistence curve.

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СИНГУЛЯРНІСТЬ ДІАМЕТРА БІНОДАЛІ В ТЕРМІНАХ ЕНТРОПІЯ–ТЕМПЕРАТУРА ДЛЯ АТОМАРНИХ ТА МОЛЕКУЛЯРНИХ РІДИН

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Резюме

У роботі досліджено поведінку діаметра кривої співіснування атомарних та молекулярних рідин в термінах ентропія–температура у околі критичної точки. Завдяки виділенню регулярної частини виявлено наявність $|\tau|^{2\beta}$ аномалії у температурній залежності діаметра кривої співіснування в термінах ентропія–температура.