The nature of the rectilinear diameter singularity

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Abstract

The rigorous explanation for the term $|t|^{2\beta}$ in the rectilinear diameter equation is given ($t = (T_c - T)/T_c$, $\beta$ is the critical exponent for the asymptotic form of the equation of state). The optimal order parameter, for which the branches of binodal are symmetric is constructed within the canonical formalism. It is shown that the ratio of the amplitudes for the diameter singularity of the order parameter $D_1^{1-\alpha}/D_2^{2\beta}$ before $|t|^{1-\alpha}$ and $|t|^{2\beta}$, where $\alpha$ determines the behavior of the heat capacity and $\beta$ is the critical exponent of the order parameter, takes the universal character modulo nonuniversal factor which depends on the thermodynamic class of the corresponding states. The analysis of entropy for argon and water leads to $\beta = 0.33$ and the corresponding amplitude ratio $S_1^{1-\alpha}/S_2^{2\beta} \approx -3.5$.

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I. INTRODUCTION

The nature of the asymmetry of the coexistence curve in liquids and multi-component solutions has a long history, which dates back to the work of Cailletet and Matthias [1], where the empirical linear law was obtained (see also [2] and references therein). The diameter \( \varphi(d)(t) \) is determined as following:

\[
\varphi(d)(t) = \frac{1}{2}(\varphi(l)(t) + \varphi(g)(t)),
\]

where \( \varphi(i)(t) \), \( i = l, g \), are the values of the order parameter on the liquid and gas branches of the coexistence curve, considered as a function of the dimensionless temperature \( t = \frac{T-T_c}{T_c} \) (\( T_c \) is the critical temperature). According to the fluctuation theory of critical phenomena [3] \( \varphi(d)(t) \) is described by the expansions:

\[
\varphi(d)(t) = \begin{cases} 
D_1 t + D_2 t^2 + \ldots, & |t| \gg t_G \\
D_{1-\alpha}|t|^{1-\alpha} + \ldots, & |t| \ll t_G
\end{cases},
\]

where \( t_G \) is the Ginzburg temperature, and \( \alpha \) is the critical exponent for the heat capacity. The \(|t|^{1-\alpha}\) anomaly, where \( t = \frac{T-T_c}{T_c} \), of the rectilinear diameter was predicted by Widom and Rowlinson in [4]. Since \( 1 - \alpha \) is close to unit (\( \approx 0.89 \)), the influence of the singular term in [2] is expected to be essential only in the intermediate vicinity of the critical point. However, the careful analysis of experimental data for the rectilinear diameter may display another type of the critical singularity:

\[
\varphi(d)(\tau) = D_2 \beta |\tau|^{2\beta} + D_{1-\alpha}|\tau|^{1-\alpha} + D_1 \tau + D_2 \tau^2 + \ldots,
\]

where \( \beta \) is the critical exponent for coexistence curve: \( 2\beta \approx 0.654 < 1 - \alpha \) (for the review see [2]). Because of very close values of the exponents of the first three terms one needs the data of high precision to get the reliable estimates for the amplitudes \( D_i \). Here we use the temperature like variable \( \tau \), which depends on the reduced temperature \( t \) and will be specified below.

The rectilinear diameter singularity has intensively discussed in [3, 4] in connection with the nature of \(|t|^{1-\alpha}\) anomaly and its relation with the Yang-Yang (YY) singularity [7]. As was shown in [8] the appearance of the \(|t|^{2\beta}\) term in the rectilinear diameter demands that the equation of state is as following:

\[
\pi(\zeta, \tau) = \pi_0 + \tau^{2-\alpha} f_{\pm} \left( \frac{\zeta}{\tau^{\beta+\gamma}} \right), \quad \tau = \tau(P, T, \mu), \quad \zeta = \zeta(P, T, \mu),
\]

where \( \pi \) is the chemical potential, \( \pi_0 \) is the regular part of the chemical potential, \( \tau \) is the temperature, \( \zeta \) is the chemical potential, \( P \) is the pressure, \( T \) is the temperature, \( \mu \) is the chemical potential, \( \beta \) is the critical exponent for coexistence curve, \( \gamma \) is the exponent of the anomalous term, \( f_{\pm} \) is the function of the regular part of the chemical potential, \( \zeta \) is the chemical potential, and \( \pi_0 \) is the regular part of the chemical potential.
where \( \pi, \tau \) and \( \zeta \) are the analytic functions of all three thermodynamic fields \( P, \mu, T \). Here \( \zeta \) is the field conjugated to the order parameter, which in general is not density, \( \tau \) is the “temperature-like” variable and \( \pi \) is the thermodynamic potential corresponding to them (the details see in [8]). Thus the scaling law ([4]) states that there is no preferred variable between \( P, \mu \) and \( T \) ([9]). Within the approach proposed in [5, 6] the YY anomaly as well as “\(|t|^{2\beta}\)” singularity appear as the result of the nonlinear dependence of the physical quantities on the scaling fields due to complete/pressure mixing, which is postulated. However, the regular method to construct the variables \( \zeta \) and \( \tau \) was not proposed.

Here we will not discuss the appearance of the \( |t|^{2\beta} \) due to nonlinear transformation of the laboratory order parameter (of type \( v = 1/n \), where \( n \) is the density and \( v \) is the specific volume). It is clear that e.g. for the Ising model one is free to chose the “non symmetrical” order parameter \( \tilde{m} = m + \gamma_2 m^2 \), where \( m \) is the magnetization, which gives the corresponding \( \tau^{2\beta} \) term for the rectilinear diameter. The choice of the proper order parameter in binary mixtures which restores the symmetry of the binodal was discussed in [10, 11], though any procedure for constructing such an order parameter was not given. The problem is to find such a microscopic observable \( \eta \) so that:

\[
\langle \eta \rangle_1 = - \langle \eta \rangle_2
\]

along the coexistence curve. Then in the framework of the RG theory the asymptotic equation of state is fully symmetrical:

\[
\langle \eta \rangle = \pm \tau^\beta g_s \left( \frac{h}{\tau^{\beta+\gamma}} \right)
\]

where \( h \) and \( \tau \) are the external field and temperature like scaling fields correspondingly. However the direct comparison of the theoretical prediction with the experimental data is impossible since the explicit form of the order parameter \( \eta \) and the fields \( h \) and \( \tau \) remain to be unstated.

The symmetrical form of the Eq. (5) is based on the symmetry property of the effective Hamiltonian \( H[\varphi(r)] = H[-\varphi(r)] \) along the binodal. In particular the Landau-Ginzburg Hamiltonian satisfies this condition [3].

In this paper we give the rigorous formalism for the construction of the scaling fields \( \tau \) and \( h \). Within such a formalism the nonlinear mixing of the laboratory fields arises naturally. In particular we show that both \( |t|^{2\beta} \) and \( |t|^{1-\alpha} \) anomalies are of the same nature.
Further we demonstrate this statement using the entropy as the order parameter. It is natural that the entropy is more sensitive to the asymmetry in the “particle-hole” configuration than the density. The latter is just the average of 1-particle distribution function for the particles.

The canonical transformation $\varphi \to \eta(\varphi)$ of the initial (laboratory) order parameter $\varphi$ is the central point of the proposed approach. Due to this the local part of the fluctuation Hamiltonian of liquids reduces to the canonical form, which is identical to the local part of the Landau-Ginzburg (LG) Hamiltonian. In canonical variables the coexistence curve is fully symmetrical, as it takes place for the Ising model. The non-zero values of the rectilinear diameter arise as the result of the inverse transformation $\eta \to \varphi$ to the laboratory order parameter. In the framework of the canonical formalism the isomorphism of critical fluctuations in liquids and the Ising model is manifested in the similarity of their thermodynamic potentials as well as their Hamiltonians. Within the perturbative approach it can be shown that the asymmetry in main order depends on the value of the coefficient $a_5$ at $\varphi^5$ term in the initial Hamiltonian. This is accordance with the results of [12].

The construction of the canonical order parameter $\eta$ for which $\eta^{(d)} = 0$ is discussed below.

II. CANONICAL FORMALISM

The Hamiltonian for the real fluids can be represented as following:

$$H[\varphi(r)] = \int (h_l(\varphi(r)) + h_{ql}(\varphi(r))) \, dV.$$  

(6)

where

$$h_l(\varphi(r)) = \sum_{n=1}^{\infty} \frac{a_n}{n} \varphi^n(r)$$

is the local density and

$$h_{ql}(\varphi(r)) = \sum_{n=1}^{\infty} \frac{a_{n,2}}{n} \varphi^n (\nabla \varphi)^2$$

is the quasilocal part in small gradient approximation. The Hamiltonian (6) includes odd power terms of the order parameter responsible for the “asymmetry effect” in the critical behavior of the system. It should be noted that there are two kinds of asymmetry terms in the Hamiltonian. They are the local and the quasilocal terms of odd powers. The importance of the lasts for the RDS was shown in [12, 13].
Note that the local term $\varphi^5$ leads to the mixing of the initial thermodynamic variables $\mu$ and $T$. The quasilocal term $\varphi(\nabla \varphi)^2$ leads to the $1 - \alpha$ singularity of the rectilinear diameter, though $2\beta$ anomaly was not obtained there.

Now let us appeal to the ideology of the Catastrophe Theory. It gives the ground to reduce the initial Hamiltonian given by the infinite series Eq. (6) to the canonical form. For this purpose the order parameter should be subjected to the so-called local canonical transformation

$$
\eta(r) = \varphi(r) + \frac{1}{2} \Gamma_2 \varphi^2(r) + \frac{1}{3} \Gamma_3 \varphi^3(r) \ldots .
$$

As a result the local density of the Hamiltonian takes the form:

$$
h^{(can)}_i(\eta) = A_1 \eta(r) + \frac{A_2}{2} \eta^2(r) + \frac{A_4}{4} \eta^4(r).
$$

with $A_4 = const$. Using the procedure described in [14] one can show that

$$
\Gamma_2 = A_1 - a_1,
$$

$$
\Gamma_3 = \frac{1}{2} A_2 - \frac{1}{2} A_1^2 + \frac{3}{2} a_1 \Gamma_2 - \frac{1}{2} a_2 + \frac{1}{2} a_1^2 + \frac{3}{2} \Gamma_2^2,
$$

$$
\Gamma_4 = -\frac{1}{2} A_1 A_2 + \frac{1}{6} A_1^3 - \frac{5}{2} a_1 \Gamma_2^2
$$

$$
+ a_2 \Gamma_2 - a_1^2 \Gamma_2 + \frac{4}{3} a_1 \Gamma_3 - \frac{1}{3} a_3 + \frac{1}{2} a_1 a_2
$$

$$
- \frac{1}{6} a_1^3 - \frac{5}{2} \Gamma_2^2 + \frac{10}{3} \Gamma_3 \Gamma_2,
$$

In this paper we illustrate the explicit construction of the transformation (7) which reduce only the local part of the Hamiltonian to the canonical form. In such a case the coefficients $A_1$ and $A_2$ should vanish simultaneously with $a_1$ and $a_2$:

$$
A_1 = 0, \quad A_2 = 0 \Leftrightarrow a_1 = 0, \quad a_2 = 0.
$$

These conditions correspond to the invariance of the locus of the CP in mean-field approximation.

To find the explicit expressions for the coefficients $A_1$, $A_2$ and $A_4$ we demand the fulfillment of the following conditions: a) the conservation of the local partition function:

$$
\int_{-\infty}^{\infty} dx \exp \left(-h^{(can)}_{loc}(x) \right) = \int_{-\infty}^{\infty} dy \exp \left(-h^{(can)}_{loc}(y) \right).
$$

(12)
b) one-to-one correspondence (bijectivity) of the canonical transformation (7):

$$\int_{-\infty}^{\eta} \exp \left(-h_{\text{loc}}^{\text{(can)}}(z)\right) dz = \int_{-\infty}^{\varphi} \exp (-h_{l}(z)) dz , \quad (13)$$

c) the condition of the invariance of the phase coexistence line $f(a_1, a_2) = 0$, which in the canonical variables is represented by the equation $A_1 = 0$.

Note that similar idea of transformation of the variable reducing the density distribution function to simpler (gaussian) form was used in [15]. In fact the existence of such a transformation is guaranteed by the Radon-Nikodim theorem [16].

Basing on these conditions one can show (see some details in [14]) that the coefficients of the canonical form satisfy the relations: as:

$$A_4 = \frac{\pi^4}{\left(\Gamma (3/4) \int_{-\infty}^{\infty} dy \exp \left(-\sum_{n=4}^{\infty} \frac{a_n}{n} y^n\right)\right)^{\frac{1}{2}}}, \quad (14)$$

$$\sqrt{\frac{A_2}{A_4}} e^{\frac{A_2}{2A_4}} K_4 \left(\frac{A_2}{2A_4}\right) = \left. \int_{-\infty}^{+\infty} \exp (-h_{l}(z)) dz \right|_{f(a_1,a_2)=0}. \quad (15)$$

Here $K_n$ is the McDonald function of $n$-th kind and $\Gamma(x)$ is the Euler gamma function [17].

Neglecting the variation of nonlocal part for the fluctuation part of the Hamiltonian and after the rescaling we get the Landau-Ginzburg (LG) form:

$$H_{\text{LG}}[\eta(r)] = \int \left( A_1 \eta(r) + \frac{A_2}{2} \eta^2(r) + \frac{A_4}{4} \eta^4(r) + \frac{1}{2} (\nabla \eta(r))^2 \right) dV , \quad (16)$$

equivalent to the Hamiltonian of the Ising model. Thus the possibility to transform the Hamiltonian to the canonical form (8) is equivalent to the isomorphism of the critical behavior of liquids with that for the Ising model. Usually, for the liquids the Hamiltonian (8) is obtained via grand canonical ensemble, which means that the coefficients $a_i$ and $A_i$ are analytic functions of the thermodynamic variables $\mu$ and $T$ [18].

Applying the standard scaling arguments (see [3, 19]) to the canonical Hamiltonian (8) we get the fluctuation contribution to the thermodynamic potential:

$$\Phi(A_1, A_2) = \Phi_0 + |A_2|^{2-\alpha} f_s \left( \frac{A_1}{|A_2|^{\beta+\gamma}} \right) \quad (17)$$

Here $\Phi$ is the thermodynamic potential which corresponds to the canonical coordinates $A_1, A_2$, which can be considered as the generalized external field and the temperature conjugated to the canonical order parameter $\eta$. The potential $\Phi$ does not coincide with the
pressure since the order parameter $\eta$ conjugated to it is not the density. The potential $\Phi$ is rather the function of all three variables $P, T, \mu$ and corresponds to Eq. (4). Of course, one can choose another set of variables, e.g. $P, T$. It is in accordance with the $P, \mu, T$ invariance hypothesis mentioned above and lead as was shown in [8] to the $"t^{2\beta}"$ anomaly in the rectilinear diameter of the density and as well as the entropy. We show below that the canonical formalism explicitly shows that both $2\beta$ and $1 - \alpha$ singularities of the rectilinear diameter of the density as the order parameter are of the same nature. They are generated by the asymmetry of the initial Hamiltonian.

Note that the local transformation generates also the quasilocal term $\eta(\nabla \eta)^2$ multiplied by the coefficient which is proportional to $\Gamma_2$. In this case all local odd power terms as well as the term $\eta(\nabla \eta)^2$ can be canceled. The coefficient $A_4$ is determined by the last condition. It means that the condition of the invariance of the mean-field critical point Eq. (11) is not assumed. The coefficients $A_1$ and $A_2$ are correspondingly modified, which lead to the shift of the mean-field critical point. The appearance of such shift is connected with the inclusion of the quasilocal interaction between modes of the order parameter. It is necessary to emphasize that this shift arises before the renormalization procedure. The detailed analysis will be the subject of separate work.

III. CANONICAL FORM FOR VAN DER WAALS EOS

Let us obtain the explicit expressions for the coefficients of the canonical form of the Hamiltonian for a case, when 1) the density of the local Hamiltonian has the truncated $\varphi^6$-form:

$$h_l(\varphi) = \sum_{n=1}^{6} \frac{a_n}{n} \varphi^n,$$

2) the coefficients $a_n$ are taken from the van der Waals equation of state:

$$p(v, t) = \frac{t}{v - 1/3} - \frac{9}{8v^2},$$

where $p$, $v$ and $t$ are the dimensionless pressure, the specific volume and the temperature

$$p = P/P_c, \quad t = T/T_c, \quad v = V/V_c$$

reduced to the coordinate of the vdW critical point (see e.g. [20]). It can be shown that:

$$a_1 = \frac{p - 1 + 4\tau}{1 + \tau}, \quad a_2 = 3\frac{\tau}{1 + \tau}, \quad a_3 = -3\frac{\tau}{1 + \tau}, \quad a_4 = \frac{3}{2}1 + 9\tau$$
\(a_5 = -\frac{21}{4} \frac{1 + \frac{81}{33} \tau}{1 + \tau}, \quad a_6 = \frac{99}{8} \frac{1 + \frac{81}{33} \tau}{1 + \tau}\).

Applying the procedure described above we get:

\[A_4 \approx a_4^{(0)} + 1.35 \frac{a_6^{(0)}}{\sqrt{a_4^{(0)}}} \approx 15.2\]  \hspace{1cm} (19)

where \(a_n^{(0)}\) is the value of the coefficient at the critical point. Other coefficients are as following:

\[A_1 \approx a_1 + \frac{2}{3\sqrt{\pi}} \frac{a_3}{\sqrt{a_4^{(0)}}} + \frac{2}{5} \frac{a_5^{(0)}}{a_4^{(0)}}, \quad A_2 \approx a_2.\]  \hspace{1cm} (20)

From Eq. (9) and Eq. (20) it follows that

\[\Gamma_2 \approx \frac{2}{5} a_5^{(0)} \left(1 + \frac{5}{3\sqrt{\pi}} \frac{a_3}{a_5^{(0)} \sqrt{a_4^{(0)}}}\right).\]  \hspace{1cm} (21)

It is necessary to emphasize that these estimations are valid only in the mean field approximation. For the accurate account of the fluctuational effects the quasilocal part of the Hamiltonian should be also taken into consideration \[12\].

**IV. THE \(2\beta\) RECTILINEAR DIAMETER SINGULARITY WITHIN THE CANONICAL FORMALISM**

The coexistence curve determined by \(A_1(\mu, T) = 0\) in the variables \((A_1, A_2, \eta)\) is naturally symmetrical. The canonical order parameter average value \(\langle \eta \rangle\) in accordance with Eq. (17) and the thermodynamics is:

\[\langle \eta \rangle = -\frac{\partial \Phi}{\partial A_1} \bigg|_{A_1=0} = \pm |\tilde{\tau}|^\beta g_s(0) + \ldots, \quad \tilde{\tau} = A_2|_{A_1=0} = a t + o(t),\]  \hspace{1cm} (22)

where \(g_s(x) = f_s'(x)\). The function \(f_s(x)\) possesses obvious symmetry \(f_s(x) = f_s(-x)\), which means that in the canonical variables the “particle-hole” symmetry is restored. The situation changes if we return to the initial order parameter:

\[\varphi = \eta - \frac{1}{2} \Gamma_2 \eta^2 + \ldots.\]

Since \(\eta\) is the symmetrical order parameter, for the rectilinear diameter \(\varphi^{(d)}\) we get:

\[\varphi^{(d)} = -\frac{1}{2} \Gamma_2 \langle \eta^2 \rangle + O\left(\langle \eta^4 \rangle\right).\]  \hspace{1cm} (23)
From Eq. (23) and the short distance behavior of the correlator \( G(r) = \langle \eta(r) \eta(0) \rangle - \langle \eta(r) \rangle \langle \eta(0) \rangle \) for the order parameter of the LG Hamiltonian (1) which determines the critical behavior of the fluctuation \( \langle \eta^2 \rangle - \langle \eta \rangle^2 \) (see e.g. [3, 21]):

\[
\langle \eta^2 \rangle - \langle \eta \rangle^2 = G(r \to 0) = \int G(k) \, dk \sim l_s(0) \, A_2^{1-\alpha} + \text{less singular terms}
\]

where \( l_s(0) \) is some constant. Therefore, along the coexistence curve we obtain:

\[
\varphi^{(d)} = -\frac{1}{2} \tilde{\Gamma}_2 \left[ g_s^2(0)|\tilde{\tau}|^{2\beta} + l_s(0)|\tilde{\tau}|^{1-\alpha} \right] + \text{less singular terms}, \tag{25}
\]

where \( \tilde{\Gamma}_2 \) the value of corresponding quantity along the coexistence curve:

\[
\tilde{\Gamma}_2 = \Gamma_2 |_{A_1=0}. \tag{26}
\]

Thus the amplitudes \( D_i \) are:

\[
D_{1-\alpha} = -\frac{1}{2} \tilde{\Gamma}_2 l_s(0), \quad D_{2\beta} = -\frac{1}{2} \tilde{\Gamma}_2 g_s^2(0). \tag{27}
\]

and either both zero or nonzeroth. Note that within such an approach both \( \tilde{\tau}^{1-\alpha} \) and \( \tilde{\tau}^{2\beta} \) anomalies contribute to the rectilinear diameter for any parameter of state \( \varphi \) chosen as the initial order parameter, e.g. entropy, density, dielectric permittivity etc. Thus we state that these anomalous terms are of the same general nature and should be treated simultaneously for the “nondegenerate” systems in terms of the Catastrophe Theory. They appear as the defect of the improper choice of the order parameter and are generated by the asymmetrical part of the Hamiltonian. This is different from the result of work [3] where \( t^{2\beta} \) anomaly is due to nonlinear mixing while \( t^{1-\alpha} \) anomaly is due to the linear mixing of the fields.

It is important to note that all results discussed in this Section do not depend on the method for the determination of the coefficient \( \Gamma_2 \). In general case \( \Gamma_2 \) determined by the contributions generated by both local and quasilocal terms in the initial Hamiltonian.

Note that since \( l_s(0) < 0 \) (see [3]), the amplitudes \( D_{1-\alpha} \) and \( D_{2\beta} \) are of opposite signs. It is important that their ratio is universal:

\[
\frac{D_{1-\alpha}}{D_{2\beta}} = \frac{l_s(0)}{g_s^2(0)} < 0. \tag{28}
\]

Processing the experimental data is usually performed in terms of the reduced temperature variable \( t \), i.e. in Eq. (25) the change \( \tilde{\tau} \to t \) is made. Therefore the ratio of corresponding amplitudes

\[
D_{1-\alpha}^{(t)} = D_{1-\alpha} \, a^{1-\alpha}, \quad D_{2\beta}^{(t)} = D_{2\beta} \, a^{2\beta} \tag{29}
\]
is non universal because of Eq. (26). Therefore the ratio is as following:

\[
\frac{D_{1-\alpha}^{(t)}}{D_{2\beta}^{(t)}} \simeq a^{1-\alpha-2\beta} \frac{l_s(0)}{g_s^{2}(0)}.
\] (30)

where the nonuniversal factor \( a \) is given by Eq. (22). The values of the amplitudes \( D_{2\beta} \) and \( D_{1-\alpha} \) depend on \( \tilde{\Gamma}_2 \). The latter can be either positive or negative depending on the details of the intermolecular interactions. This may explain the fact that for molecular liquids \( D_{2\beta} > 0 \) while in the case of liquid metals the opposite sign takes place \[22, 23\]. This may attributed to the difference in the short range interaction in these systems. For the molecular fluids the pure hard core interaction takes place while in liquid metals the polarizability effects are essential due to incomplete electronic shells e.g. in liquid \( Hg \) \[24, 25\]. Strong polarizational effects in liquid metals and ionic fluids give rise to screening and the formation of bound states (dimers, trimers etc.). In such a situation one can expect that the quasilocal part of the Hamiltonian for such systems differs very much from that of molecular liquids because of strong dispersive interparticle interactions.

Though the functional form \( \tilde{\tau}(t) \) is non universal, it is the same for the systems, which obey the law of corresponding states. This inference is in correspondence with the estimates made in \[22\] for molecular and ionic liquids for which the density as the order parameter was used:

\[
\frac{D_{1-\alpha}}{D_{2\beta}} \approx -10.
\] (31)

V. ANALYSIS OF THE DATA FOR ARGON AND WATER

To confirm the results obtained we have analyzed the experimental data on the entropy \( s \) for water and its saturated vapor \[26\] (see Fig. 1). In this case the initial order parameter \( \varphi \) is naturally defined as \( \varphi = \frac{4\pi\rho}{4\pi\rho} \). It is natural that the entropy is more sensitive to the configuration “hole-particle” than the density, which is just the average of 1-particle distribution function.

The evaporation heat \( q \) and rectilinear diameter \( S^{(d)} \) are determined in the standard way:

\[
q = T_c s_c(\varphi^{(g)} - \varphi^{(l)}) \quad \text{and} \quad S_d(t) = \frac{1}{2}(S^{(g)} + S^{(l)}). \]

The behavior of \( \varphi^{(d)} \) for water and argon is presented in Fig. 1. In accordance with said above the corresponding experimental data were fitted by the formulas:

\[
\frac{q}{T_c s_c} = q_1 |t|^\beta + q_2 |t|^{\beta+\Delta} + q_3 t + o(t)
\] (32)
FIG. 1: The rectilinear diameter of entropy for water (solid) and argon (points) according to data of [26].

and

\[ S^{(d)}(t) = S_2^{(t)}|t|^{2\beta} + S_1^{(t)}|t|^{1-\alpha} + S_1^{(t)}t + o(t). \]  \hspace{1cm} (33)

Note, that as follows from the representation:

\[ S = c_v \ln T + f(n) \]  \hspace{1cm} (34)

\( S_{1-\alpha} < 0 \). In contrast to the coefficients \( D_{1-\alpha} \) which is generated by the asymmetry of the Hamiltonian, the coefficient \( S_{1-\alpha} \) does not vanish in symmetrical case, e.g. in the Ising model, and correspondingly:

\[ S_1^{(t)} = S_1^{(sym)} + S_1^{(asym)}. \]  \hspace{1cm} (35)

It is obvious that the symmetrical part \( S_1^{(sym)} \) is generated by the heat capacity singularity. The asymmetrical part of the amplitude is of the same structure as Eq. (29) with corresponding ratio (31). At that we put \( \alpha \) and \( \Delta \) to be known: \( \alpha = 0.11 \) and \( \Delta = 0.5 \). The analysis shows that \( \beta \) is the essential function of the temperature interval \( t_{exp} \), inside which the experimental data were taken into account. The fitting was performed for \( \beta \) and the coefficients \( q_i, S_i \) in order to achieve the minimum for the standard deviation. The value of such a minimum depends on the interval of interpolation. Both for argon and water the optimal interval corresponded to \( 0 < t < t_* \) with \( t_* \approx 0.2 \) with close values of coefficients though the data set for argon is smaller than that of water. The ratio (30) both for argon
and water takes close values:

\[
\frac{S_1^{(Ar)}}{S_2^{(Ar)}} \approx -3.4, \quad \frac{S_1^{(W)}}{S_2^{(W)}} \approx -3.7, \tag{36}
\]

which is in correspondence with the result (28). The difference is attributed to the nonuniversal factor \(a\) (see Eq. (26)) which depends on the details of the canonical transformation. In order to distinguish between the \(t^{2\beta}\) and \(t^{1-\alpha}\) terms for rectilinear diameter of the density we subtracted the analytic background terms taking into account the data beyond the region \(t > t_G\). Such a subtracting allow to fix approximately the value \(t_G\) because the linear analytic term is important even in fluctuational region. We fit the data in the region \(t > t^*\) with the Taylor expansion in \(t\) up to \(t^5\) order and check the difference between this regular expansion and the data. At \(t^* > 0.2\) no significant deviation between them was detected. Therefore we can conclude that the crossover takes place at \(t_G \approx 0.2\).

It should be noted that it is impossible to fit the data with the the singular \(t^{1-\alpha}\)-term only. The \(t^{2\beta}\)-term is essential and together with the analytical terms allows to fit the data within rather broad interval \(0 < t < 0.2\) correctly both for the argon and water. Note that in approach used \[27, 28\] in the Ginzburg temperature depends on the choice of the order parameter and may differ substantially depending on the choice of the truncated expansion for the initial Hamiltonian.

Note that the existence of additional \(t^{2\beta}\) term is also implicitly assumed in empirical equation of state for water of Wagner&Pruss, which fits the data in whole coexistence region up to the triple point with the value \(\beta = 0.33\), though the term \(\sim t^{1-\alpha}\) was not taken into account \[26\]. From this point of view the equations of state in broad interval, which uses the crossover functions are preferable \[27, 29\].

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