Comparison of the scaling models for substance densities along saturation line

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Abstract. We discuss various thermodynamic equations used to represent the properties along the saturation line (fluid density, gas density, order parameter, mean diameter, etc) in a neighborhood of the critical temperature Tc. These properties are described scaling functions, depending on some parameters including the critical exponents α and β. Along with well—known models, we investigate a new model that represents the mean diameter as a sum of two scaling members in the critical region. The first term of this sum depends on the exponent, α and the second one depends on exponent, 2β. In the paper is given a methodological rationale for the new function representing the mean diameter. We have made numerical estimates for sulphur hexafluoride using the parameters involving with the above scaling equations.

1. Introduction

One of the most urgent problems is connected with a construction of thermodynamic functions (the liquid density (ρl), the gas density (ρg) of the order parameter (fs), the mean diameter (fd) etc) in a specified neighborhood of the critical temperature Tc. The problem plays an important role in the scale theory of critical phenomena (MT). These thermodynamic functions depend on the critical exponents, α, β, as well as they must follow to a number of the MT conditions, including:

(i) the indexes, α, β, are universal for all substances,
(ii) α exponent is universal not only for the mentioned functions, but also for the saturation pressure (P) and isochoric heat capacity (Cv).

Our analysis shows that the different values of the critical exponent α = (α1, α2, ... ) used in the literature. For example, in common prior to 2000 scaling model of Wegner [1] uses the following series

\[ f_s = (\rho_l - \rho_g) (2\rho_c)^{-1} = B_{d0} \tau^{\beta_1} + B_{d1} \tau^{\beta_1+\Delta}, \]

\[ f_d = (\rho_l + \rho_g) (2\rho_c)^{-1} - 1 = B_{d0} \tau^{1-\alpha_1} + B_{d1} \tau^{1-\alpha_1+\Delta} + B_{d2} \tau, \]
where $\alpha = 0.109$, $\beta = 0.325$—the exponents those follow from the MT and have an error estimated as $\sim 0.1\%$ [2], $\Delta = 0.5$ is an amendment for the first non asymptotic member, $(B_{sl}, B_{sl})$—coefficients determined by a statistical processing of experimental data.

It is important that equation (2) contains the singular member $B_{d0}\tau^{1-\alpha_1}$ that is the derivative $d\rho^2/d\tau^2$ is singular ($d\rho^2/d\tau^2 \approx B_{d0}\tau^{1-\alpha_1} \rightarrow -\infty$ when $\tau \rightarrow 0$, the parameter $\alpha_1$ is small). Earlier, the first theoretical step in the construction of the functions $(\rho, \rho_1, f_2, f_3, \cdots)$ has been made by Landau [2, 3]. He has used a special decomposition of the function $g$ (the free energy density), which contains the arguments (the relative density $(\Delta \rho = \rho/\rho_c - 1)$, $\tau$). He has suggested the following expression of $\Delta \rho$ in the vicinity of the critical point

$$\Delta \rho_{g,l} = \pm (a/c) \tau^{\beta_2} + (b/(2c)) \tau^{1-\alpha_2} = \pm f_s + f_d = \pm B_{s0}\tau^{\beta_2} + B_{d0}\tau^{1-\alpha_2}, \quad (3)$$

where $\Delta \rho_{g}$ and the sign “−” relate to gas branch, $\Delta \rho_{l}$ and the sign “+” relate to the liquid branch, $\alpha_2 = 0$ and $\beta_2 = 0.5$ are theoretical values of the critical exponents obtained by Landau [3].

Equation (3) contains other values of $\alpha_2$ and $\beta_2$ in comparison to equations (1), (2). This equation reflects a Landau hypothesis, $H_L$, in the following form:

(i) equation (3) must contain six parameters ($B_{d0}, B_{s0}, \rho_c, T_c, \beta_2, \alpha_2$), while $\beta_2$ and $\alpha_2$ are not dependent on substances,

(ii) it includes a linear term ($\alpha_2 = 0$) and does not contain a scaling member in $f_d$ with an index $1 > \alpha > 0$,

(iii) it has positive coefficients $B_{d0} > 0$ and $B_{s0} > 0$.

It is shown in [4] that $f_d (3)$ must include $\alpha_2 \approx 0.1$. The authors accepted that $c = c_1 \tau^v$ and $v \approx 0.1$ and got

$$\Delta \rho_{g,l} = \pm \left[(a/c)^{0.5} \tau^{(1-v)/2}\right] + \left[b/(2c)\right] \tau^{(1-v)} = \pm \left(B_{s0}\tau^{\beta_2}\right) + B_{d0}\tau^{2\beta_2}, \quad (4)$$

$$f_s = B_{s0}\tau^{\beta_2}, \quad f_d = B_{d0}\tau^{2\beta_2}, \quad (5)$$

where $\beta_2 = (1 - v)/2$.

Model (5) is accepted as the hypothesis, $H_{ML}$, and meets the following conditions:

(i) it contains only five parameters ($B_{d0}, B_{s0}, \rho_c, T_c, \beta_2$),

(ii) it does not include a linear member,

(iii) it has positive coefficients $B_{d0} > 0, B_{s0} > 0$.

If the exponent takes values as $\alpha_2 = (0, 0.11, 0.15, 0.333)$, then it follows from equation (5) that the corresponding $\beta_2$ values are equal to $\beta_2 = (0.5, 0.445, 0.425, 0.333)$.

These functions have been investigated in a great number of papers, where numerical data on parameters ($B_{d0}, B_{s0}, \rho_c, T_c, \beta_2, \alpha$) are placed for a wide range of substances. So, in 1990 Anisimov [2] has developed a model that includes $\alpha_1$ and $\beta_1$, proposed by Wegner [1]. His model has a satisfactory accuracy in the interval $\tau_{low} \cdots \tau_{high} = 10^{-4} \cdots 10^{-2}$ for H2O and is written in the form

$$f_s = B_{s1}\tau^{\beta_1} + B_{s1}\tau^{\beta_1+\Delta}, \quad (6)$$

$$f_d = B_{d1}\tau^{1-\alpha_1} + B_{d1}\tau, \quad (7)$$

where $B_{sl}, B_{sl}$—coefficients determined by a statistical processing of experimental data on the densities of H2O.

A new hypothesis ($H_A$) connects the diameter, $f_d$, with the chemical potential, $\mu$, entropy, $s$, specific heat, $C_v$, and the saturation pressure $P$. The $H_A$ has been developed from 2003 to 2015.
in a few works including [5–7]. In accordance with the $H_A$, Anisimov [5] has got the numerical data of $f_d$ diameter written in the form

$$f_d = B_{d0} \tau^{-1-\alpha_1} + B_{d1} \tau + B_{d2} \tau^{2\beta_1}.$$  \hspace{1cm} (8)

Equation (8) satisfies the following conditions:

(i) contains an additional singular term $B_{d2} \tau^{2\beta_1}$,

(ii) includes a linear term,

(iii) the exponents $\alpha_1$ and $\beta_1$ meet the following condition: $1 > 1 - \alpha_1 > 2\beta_1$ (2$\beta_1 = 0.65$, $1 - \alpha_1 = 0.89$),

(iv) the values of $\alpha_1$ and $\beta_1$ chosen as theoretical ones.

These conditions lead to the conclusion that the second scaling member is dominant over others in some small region $0 < \tau < \tau_A$. Equations (6) and (8) take the following form in this range

$$f_s = B_{s0} \tau^{\beta_1}, \quad f_d = B_{d2} \tau^{2\beta_1}.$$ \hspace{1cm} (9)

The derivative $df_d/dT$ is singular ($df_d/dT \approx \tau^{2\beta_1-1}$ for $\tau \to 0$) for equations (8) and (9). Equations (9) and (4) are similar in the shape: the exponent $\beta_1$ included in the diameter $f_d$ (equation (9)) with factor of two. Numerical data on the parameters ($B_{d0}$, $B_{d1}$, $B_{d2}$) included in equation (8) obtained in [5] for a number of substances, including SF$_6$ and N$_2$ in the range $\tau_{low} \cdots \tau_{high} = 10^{-4} \cdots 10^{-2}$. At the same time in their calculations, the authors of [5] attracted the experimental data on such properties along the saturation line as density $\rho$, specific heat $C_v$ and pressure $P$. M. Fisher introduced the term “complete scaling” within the $H_A$ hypothesis in the pioneering work [7]. Equation (8) has an aim to improve $f_d$ structure and to increase $f_d$ accuracy. It reflects current trends MT. Thus, the second scaling member first introduced in the model (8).

Note firstly, that the experimental critical exponents ($\alpha_{exp}$, $\beta_{exp}$) are presented in literature and obtained by statistical processing of the experimental data for a wide range of substances. These values significantly different from the theoretical values of $\alpha$ and $\beta$ mentioned above. The values of $\alpha_{exp}$ are given in references [2, 4, 8, 9] and cover a whole range $\alpha_{exp} = 0.10 \cdots 0.14$.

Thirdly, there are almost no experimental values of the parameters ($\alpha$, $\beta$, $B_{d0}$, $B_{d1}$, $B_{d2}$) within the diameter $f_d$ (equation (8)).

Fourthly, a wide range of values of $\alpha$ and $\beta$, presented in literature, talks about the important issue of “What are the values of the exponents and beta implemented in reality and how they should be used in the construction of scaling equations with respect to a new substance?”.

Fifthly, we have a task to receive methodical substantiation of equation (8) and to make numerical estimates of the parameters ($\alpha$, $\beta$, $B_{d0}$, $B_{d1}$, $B_{d2}$), included in this equation, on the basis of experimental data on the density of a test substance.

2. A correlation of the diameter, $f_d$, and chemical potentials along the saturation line

Let us consider the method of explaining the appearance of the additional singular term in equation (2), (3) and (7).

We are using differential equations of the thermodynamics to chemical potentials $\mu_g$, $\mu_l$ on the saturation line in the form

$$(d\mu_l/dT ) = v_l (dP/dT ) - s_l,$$ \hspace{1cm} (10)

$$(d\mu_g/dT ) = v_g (dP/dT ) - s_g,$$ \hspace{1cm} (11)
where \( v_g, v_l, s_g, s_l \) are the specific volumes and entropies along the saturation line.

A summation of equations (10) and (11) yields

\[
d\mu_g/dT + d\mu_l/dT = (v_g + v_l) (dP/dT) - (s_g + s_l). \tag{12}
\]

We perform some transformation using equation (12) in order to obtain expressions: a) for the sum, \( \rho_g + \rho_l \), and b) for the diameter, \( f_d \).

In the first step, we present the sum of the volumes as

\[
v_g + v_l = (\rho_g + \rho_l)/ (\rho_g \rho_l). \tag{13}
\]

In the second step, we write the sum of the densities bringing equations (12) and (13)

\[
\rho_g + \rho_l = (v_g + v_l)(\rho_g \rho_l) = (d\mu_g/dT + d\mu_l/dT + s_g + s_l) (dP/dT)^{-1} (\rho_g \rho_l). \tag{14}
\]

The third step will present the components of equation (14) those are the leading members of the scaling at small \( \tau \). For example, the terms, \( B_{s0} c_2, B_{d0} c_1^{-1} c_2, \) are taken as an initial approximation of the terms those are included in the density. We write these components on the base of formulas presented in references [2, 5, 7, 8, 10] in forms

\[
dP/dT = B_{p1} \left( 1 - B_{p0} \tau^{1-\alpha} + o(\tau) \right) \approx B_{p1} \left( 1 - B_{p0} \tau^{1-\alpha} \right), \tag{15}
\]

where \( (dP/dT)_c = B_{p1} \),

\[
d\mu_g/dT = B_{M1} (1 - B_{M0} \tau^{1-\alpha} + o(\tau)) \approx B_{M1} (1 - B_{M0} \tau^{1-\alpha}), \tag{16}
\]

where \( (d\mu_g/dT)_c = B_{M1} \),

\[
d\mu_l/dT = B_{M1} (1 - B_{M0} \tau^{1-\alpha} + o(\tau)) \approx B_{M1} (1 - B_{M0} \tau^{1-\alpha}), \tag{17}
\]

where \( (d\mu_l/dT)_c = B_{M1} \),

\[
s_g = B_{S_g} \tau^{1-\alpha} v_g + A_s + A_{s2} \tau + (B_1 + B_2 \tau) v_g + o(\tau), \tag{18}
\]

\[
s_l = B_{S_l} \tau^{1-\alpha} v_l + A_s + A_{s2} \tau + (B_1 + B_2 \tau) v_l + o(\tau) \tag{19}
\]

The connection between the chemical potential and the specific heat has the form,

\[
d^2\mu_g/dT^2 = B_{C1} C_{v_g}(\tau) = B_{C2} \tau^{-\alpha}, \tag{18}
\]

and is taken into account in equation (19). The connection was studied in [5, 7, 10].

We assume that the densities have the form \( \rho_l = \rho_c (1 + B_{s0} \tau^\beta + B_{d0} \tau^{1-\alpha}) \) and \( \rho_g = \rho_c (1 - B_{s0} \tau^\beta + B_{d0} \tau^{1-\alpha}) \) and the complex, \( (\rho_g \rho_l) \), can be written as

\[
\rho_g \rho_l = \rho_c^2 \left( 1 + 2 B_{d0} \tau^{1-\alpha} - B_{s0}^2 \tau^{2\beta} \right) \approx \rho_c^2 \left( 1 + 2 B_{d0} \tau^{1-\alpha} - B_{s0}^2 \tau^{2\beta} \right). \tag{20}
\]

In the fourth step, we write volumes \( v_l \) and \( v_g \) as

\[
v_l = 1/\rho_l = 1/(\rho_c (1 + \Delta \rho_l)) = 1/\rho_c (1 - \Delta \rho_l + \Delta \rho_l^2 + \cdots) \approx 1/\rho_c \left( 1 - B_{s0} \tau^\beta - B_{d0} \tau^{1-\alpha} + B_{s0}^2 \tau^{2\beta} \right),
\]

\[
v_g = 1/\rho_g = 1/(\rho_c (1 - \Delta \rho_g)) = 1/\rho_c (1 - \Delta \rho_g + \Delta \rho_g^2 + \cdots) \approx 1/\rho_c \left( 1 - B_{s0} \tau^\beta + B_{d0} \tau^{1-\alpha} + B_{s0}^2 \tau^{2\beta} \right).
\]

\[
\]
\[
v_g = 1/\rho_g = 1/(\rho_c (1 + \Delta \rho_g)) = 1/\rho_c \left( 1 - \Delta \rho_g + \Delta \rho_g^2 + \cdots \right) \approx 1/\rho_c \left( 1 + B_{s0} \tau^\beta - B_{d0} \tau^{1 - \alpha} + B_{s0}^2 \tau^{2\beta} \right),
\]

where \(\Delta \rho_l = B_{s0} \tau^\beta + B_{d0} \tau^{1 - \alpha}, \Delta \rho_g^2 = B_{s0}^2 \tau^{2\beta} + B_{d0} \tau^{2(1 - \alpha)} + \cdots\) is the component obtained as a quadratic term of the Maclaurin series for the factor \(1/(1 + \Delta \rho_l); \Delta \rho_g = -B_{s0} \tau^\beta + B_{d0} \tau^{1 - \alpha}\), \(\Delta \rho_g^2 = B_{s0}^2 \tau^{2\beta} + B_{d0} \tau^{2(1 - \alpha)} + \cdots\).

At the fifth step, we write the following complexes included in eqution (14)

\[
d\mu_g/dT (dP/dT)^{-1} (\rho_g \rho_l) = B_{M1} \left( 1 - B_{M0} \tau^{1 - \alpha} \right) B_{p1}^{-1} (1 + B_{p0} \tau^{1 - \alpha}) \rho_c^2 \left( 1 + 2 B_{d0} \tau^{1 - \alpha} - B_{s0}^2 \tau^{2\beta} \right) = A_{M_g} \left( 1 + B_{p0} \tau^{1 - \alpha} - B_{M0} \tau^{1 - \alpha} + \cdots \right) \left( 1 + 2 B_{d0} \tau^{1 - \alpha} - B_{s0}^2 \tau^{2\beta} \right) = A_{M_g} \left( 1 + 2 B_{d0} \tau^{1 - \alpha} - B_{s0}^2 \tau^{2\beta} + B_{p0} \tau^{1 - \alpha} + \cdots \right),
\]

where \(A_{M_f} = B_{M1} B_{p1}^{-2} \rho_c^2\).

We write complexes \(s_g (dP/dT)^{-1} (\rho_g \rho_l)\) and \(s_l (dP/dT)^{-1} (\rho_g \rho_l)\), highlighting the constants and terms containing \(\tau^{2\beta}\) function

\[
s_g (dP/dT)^{-1} (\rho_g \rho_l) = B_{S_g} \tau^{1 - \alpha} B_{p1}^{-1} (1 + B_{p0} \tau^{1 - \alpha}) \rho_l + (A_{s1} + A_{s2} \tau) B_{p1}^{-1} (1 + B_{p0} \tau^{1 - \alpha}) \rho_c^2 \left( 1 + 2 B_{d0} \tau^{1 - \alpha} - B_{s0}^2 \tau^{2\beta} \right) + (B_1 + B_2 \tau) B_{p1}^{-1} (1 + B_{p0} \tau^{1 - \alpha}) \rho_l = A_{s1} B_{p1}^{-1} \rho_c^2 + B_1 B_{p1}^{-1} \rho_l - A_{s1} B_{p1}^{-1} \rho_c^2 B_{s0}^2 \tau^{2\beta} + \cdots,
\]

\[
s_l (dP/dT)^{-1} (\rho_g \rho_l) = B_{S_l} \tau^{1 - \alpha} B_{p1}^{-1} (1 + B_{p0} \tau^{1 - \alpha}) \rho_l + (A_{s1} + A_{s2} \tau) B_{p1}^{-1} (1 + B_{p0} \tau^{1 - \alpha}) \rho_c^2 \left( 1 + 2 B_{d0} \tau^{1 - \alpha} - B_{s0}^2 \tau^{2\beta} \right) + (B_1 + B_2 \tau) B_{p1}^{-1} (1 + B_{p0} \tau^{1 - \alpha}) \rho_l = A_{s1} B_{p1}^{-1} \rho_c^2 + B_1 B_{p1}^{-1} \rho_l - A_{s1} B_{p1}^{-1} \rho_c^2 B_{s0}^2 \tau^{2\beta} + \cdots.
\]

We derive an expression for the sum of \((\rho_g + \rho_l)\), using equations (22), (23) and separating first constant and terms containing \(\tau^{2\beta}\) function as

\[
\rho_g + \rho_l = A_{M_g} \left( 1 + 2 B_{d0} \tau^{1 - \alpha} - B_{s0}^2 \tau^{2\beta} + B_{p0} \tau^{1 - \alpha} + \cdots \right) + A_{M_f} \left( 1 + 2 B_{d0} \tau^{1 - \alpha} - B_{s0}^2 \tau^{2\beta} + B_{p0} \tau^{1 - \alpha} + \cdots \right) + 2 \left( A_{s1} B_{p1}^{-1} \rho_c^2 + B_1 B_{p1}^{-1} \rho_l - A_{s1} B_{p1}^{-1} \rho_c^2 B_{s0}^2 \tau^{2\beta} \right) + \cdots,
\]

where the coefficients and parameters are related by the equation

\[
2 \rho_c = A_{M_g} + A_{M_f} + 2 \left( A_{s1} B_{p1}^{-1} \rho_c^2 + B_1 B_{p1}^{-1} \rho_l \right).
\]
We write amount \((\rho_\gamma + \rho_\iota)\), allocating first member comprising \(\tau^{2\beta}\) function in the form:

\[
\rho_\gamma + \rho_\iota = 2\rho_c + 2A_M g B_{d0} \tau^{1-\alpha} - A_M g B_{s0}^2 \tau^{2\beta} - A_M g B_{d0}^2 \tau^{2\beta} - 2A_{s1} B_{d1} \rho_c^2 B_{s0} \tau^{2\beta} + \cdots = \\
= 2\rho_c + A_{d0}\rho_c \tau^{1-\alpha} + 2A_{d2}\rho_c \tau^{2\beta} + \cdots.
\]

Using equation (26), we present the expression for \(f_d\) in the form:

\[
f_d = A_{d0}\tau^{1-\alpha} + A_{d2}\tau^{2\beta} + \cdots.
\]

This methodical approach shows that you can get a model of \(f_d\) that is consistent with the models (4) and (9): on the following grounds: this model has a singular component comprising a function \(\tau^{2\beta}\).

### 3. Numerical data of the scaling equations for sulfur hexafluoride

It is of interest to make a comparative analysis of these equations using an example of the description of the properties \((\rho_\gamma, \rho_\iota, f_s, f_d)\) for sulphur hexafluoride, which is selected as a test substance with very precise experimental \((\rho_\gamma, \rho_\iota, T)\) data [11] in the interval between \(\tau_{\text{low}} = 10^{-4}\) to \(\tau_{\text{tr}} = 0.3\). Along with this, it is necessary to solve the problem: to obtain experimental estimates for parameters of the scaling equations discussed.

At the first stage we consider the equations studied in [4, 8] and consisted of scaling \((F_\text{scale})\) and regular \((F_{\text{reg}})\) parts with the numerical parameters in relation to SF\(_6\). These equations have a form:

\[
f_s = B_{s0} \tau^{\beta_4} + B_{s1} \tau^{\beta_4 + \Delta} + B_{s2} \tau^{\beta_4 + 2\Delta} + B_{s3} \tau^2 + B_{s4} \tau^3,
\]

\[
f_d = B_{d0} \tau^{1-\alpha_4} + B_{d1} \tau^{1-\alpha_4 + \Delta} + B_{d2} \tau^{1-\alpha_4 + 2\Delta} + B_{d3} \tau^2 + B_{d4} \tau^3,
\]

where \(B_{si}, B_{di}, i = 0, 1, 2\) – coefficients related to \(F_\text{scale}\), \(B_{si}, B_{di}, i = 3, 4\) – coefficients related to \(F_{\text{reg}}\), \(\alpha_4, \beta_4\) – indices defined on the basis of statistical treatment of experimental \((\rho_\gamma, \rho_\iota, T)\)-data.

\(F_\text{scale}\) structure meets MT. Equations (28) and (29) include the optimal values of the critical parameters \((T_c, \rho_c, \alpha_4, \beta_4, B_{d0}, B_{d0})\), which are calculated with empirical coefficients \((B_{si}, B_{di})\) on the basis of experimental \((\rho_\gamma, \rho_\iota, T)\)-data and a nonlinear least square method (NLLSM) [4, 8].

Note that in equation (29) is missing the linear term in accordance with the hypothesis \(H_{\text{ML}}\); this hypothesis is used in several papers including [8, 9]. The parameters of (28) and (29) (table 1) are obtained by us using experimental \((\rho_\gamma, \rho_\iota, T)\)-data [11] of SF\(_6\). Parameters \((T_c, \rho_c, \alpha_4, \beta_4, B_{d0}, B_{d0})\) is used as an initial approximation parameters of equation (27).

In accordance with NLLSM an initial approximation for the parameters \((T_c, \rho_c, \alpha_4, \beta_4, B_{d0}, B_{d0})\) was chosen in accordance with literature data including 1) \(\alpha_4 = 1 - 2\beta_4 = 0.35\) in accordance with the hypothesis \(H_A, 2) \beta_4 = 0.325\). The proposed equations reproduce the most

### Table 1. Parameters of equations (28) and (29).

| \(\rho_c\), kg/m\(^3\) | \(T_c\), K | \(\alpha_4\) | \(\beta_4\) | \(B_{s0}\) | \(B_{s1}\) | \(B_{s2}\) | \(B_{s3}\) | \(B_{s4}\) | \(B_{d0}\) | \(B_{d1}\) | \(B_{d2}\) | \(B_{d3}\) | \(B_{d4}\) |
|----------------|-----|-------|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 742.255 | 318.709 | 0.1099 | 0.3474 | 1.9575 | -0.024777 | 0.142317 | -1.324779 | 1.60129 | 0.4695 | 0.597385 | 0.85706 | -1.250538 | 0.334847 |

We write amount \((\rho_\gamma + \rho_\iota)\), allocating first member comprising \(\tau^{2\beta}\) function in the form

\[
\rho_\gamma + \rho_\iota = 2\rho_c + 2A_M g B_{d0} \tau^{1-\alpha} - A_M g B_{s0}^2 \tau^{2\beta} - A_M g B_{d0}^2 \tau^{2\beta} - 2A_{s1} B_{d1} \rho_c^2 B_{s0} \tau^{2\beta} + \cdots = \\
= 2\rho_c + A_{d0}\rho_c \tau^{1-\alpha} + 2A_{d2}\rho_c \tau^{2\beta} + \cdots.
\]

Using equation (26), we present the expression for \(f_d\) in the form

\[
f_d = A_{d0}\tau^{1-\alpha} + A_{d2}\tau^{2\beta} + \cdots.
\]
Figure 1. An additional function $F$ and its members. 1—function $F_{\text{exp}}$, built from experimental ($\rho_g$, $\rho_l$, $T$)-data [11], 3—term $B_{d0} \tau^{2\beta_4} \rho_c$, 6—sum of terms $B_{d0} \tau^{2\beta_4} \rho_c + B_{d0} \tau^{1-\alpha_4} \rho_c$; 7—limit $F_{\text{high}}$, 8—term $B_{d0} \tau^{2\beta_4} \rho_c$, 9—term $B_{d0} \tau^{1-\alpha_4} \rho_c$.

Figure 1 shows the upper limit of acceptable values $F_{\text{high}} = F_{\text{exp}} + \Delta \rho$ (symbols 7), and the deviation of the function $F$ from $F_{\text{exp}}$ lies in the range $\Delta \rho = \pm 1.4 \text{ kg/m}^3$. It allows us to conclude that $f_d$ (29) has a small error.

In the second stage of the analysis we have introduced an additional dimension function, $F$, in the form

$$F = (\rho_g + \rho_l)/2 - \rho_c f_d = F_\alpha + F_\beta + \cdots,$$

(30)

where $F_\alpha$ and $F_\beta$—terms of (30), for example, $F_\alpha = B_{d0} \tau^{1-\alpha_4} \rho_c$—a term corresponding to the first term of the equation (29).

The analysis shows that the function $F$ can be built with the help of equation (29); this variant is in satisfactory agreement with the function $F_{\text{exp}}$ (symbols 1, figure 1) calculated on the base of experimental $(\rho_g, \rho_l, T)$-data [12], and has an error $\delta F_{\text{exp}} \approx 2\delta \rho_{\text{exp}}$, here $\delta \rho_{\text{exp}}$—error of the data [12]. The deviation of the function $F$ from $F_{\text{exp}}$ lies in the range $\Delta \rho = \pm 1.4 \text{ kg/m}^3$ at $\tau = \tau_{\text{low}} \cdots 0.3$. We have got $F$ that coordinates satisfactory (within the estimate of $\delta F_{\text{exp}}$) to equation (29) and to the values of $F_{\text{exp}}$. It allows us to conclude that $f_d$ (29) has a small error.

It can be seen in figure 1 too:

(i) the upper limit of acceptable values $F_{\text{high}} = F_{\text{exp}} + \Delta \rho$ (symbols 7),

accurate $(\rho_g, \rho_l, T)$-data [11], covering the interval from $\tau_{\text{low}}$ to $\tau_{\text{tr}}$ with a small root mean square deviation $S = 0.34\%$, which is determined on the base of deviations of experimental data from corresponding values of the density obtained on the base of (28) and (29).
(ii) information about the term $F_{\alpha} = B_{d0}\tau^{1-\alpha_4}\rho_c$ (symbols 9), which corresponds to the equation (29),

(iii) information about the term, $B_{d0}^2\tau^{2\beta_4}\rho_c$, (symbols 3), which includes the coefficient $B_{d0}$ (table 1) follows to recommendations [5].

It possible to conclude from our comparison:

(i) the term $F_{\alpha}$ coincides with the function $F_{\exp}$ at $\tau = \tau_{\text{low}} \cdots 0.01$,

(ii) the term, $B_{d0}^2\tau^{2\beta_4}\rho_c$, is substantially higher than the function $F_{\exp}$ at $\tau = \tau_{\text{low}} \cdots 0.3$,

(iii) the term, $B_{d0}^2\tau^{2\beta_4}$, can not be included in the equation (29) along with the term $B_{d0}\tau^{1-\alpha_4}$, since this amount is several times greater than $f_{\exp}$.

The experimental values of $F_{\exp}$ give some option for the empirical determination of the term $F_{\exp}$, which can be complementary to the term $F_{\alpha}$ and to obtain the value of the function $F_{\text{opt}} = F_{\alpha} + F_{\beta_{\exp}}$ calculated and satisfactorily consistent with the values $F_{\exp}$. We have considered a term $F_{\beta_{\exp}} = B_{d_{\exp}}\tau^{2\beta_4}\rho_c$ (symbol 8), which meets the following conditions:

(i) $B_{d_{\exp}} = 0.0518$,

(ii) sum $B_{d_{\exp}}\tau^{2\beta_4}\rho_c + B_{d0}\tau^{1-\alpha_4}\rho_c$ represents the function $F_{\text{opt}}$ (symbol 6); it locates between the function $F_{\exp}$ and the limit $F_{\text{high}}$;

(iii) the term $F_{\beta_{\exp}}$ (symbols 8) intersects the term $F_{\alpha}$ (symbols 9) when $\tau = 3 \times 10^{-5}$; the term $F_{\beta_{\exp}}$ is a liding term compared to term $F_{\alpha}$ at smaller $\tau$; it is possible to accept that there is a temperature limit $\tau_A = 3 \times 10^{-5}$; $f_d$ has the form $f_d \approx B_{d_{\exp}}\tau^{2\beta_4} > B_{d0}\tau^{1-\alpha_4}$ at $\tau < \tau_A$.

(iv) $\cdot\cdot\cdot f_{d_{\exp}}/d\tau \approx B_{d_{\exp}}\tau^{2\beta_4-1} \rightarrow \infty$ for $\tau \rightarrow 0$.

Note, firstly, that the function $F_{\text{opt}}$ is higher than the term $F_{\alpha}$ at $\tau = \tau_{\text{low}} \cdots 0.01$, but not beyond the margin of the error, $\Delta \rho = 1.4$ kg/m$^3$. Secondly, a quantitative characterization of the functions $F_{\text{opt}}$ is represented by values calculated in test point at $\tau = 0.008498$ ($F_{\text{opt}} = 6.4022$ kg/m$^3$, $F_{\alpha} = B_{d0}\tau^{1-\alpha_4} = 5.002$ kg/m$^3$, $F_{\beta} = B_{d_{\exp}}\tau^{2\beta_4}\rho_c = 1.40$ kg/m$^3$, $F_{\exp} = 5.4275$ kg/m$^3$, $\rho_l = 1025$ kg/m$^3$, $\rho_g = 470.825$ kg/m$^3$, $T = 316.00$ To), and the deviation $F_{\text{opt}}$ from values $F_{\exp}$ does not exceed the tolerance $\Delta \rho = 1.4$ kg/m$^3$.

Thirdly, the comparison of the equations let us conclude: (a) the function $F_{\exp}$ ($(\rho_g, \rho_l, T)$-points [12]) located systematically higher than the function $F_{\exp}$ ($(\rho_g, \rho_l, T)$-points [11]); so, this deviation is 1.1 kg/m$^3$ at $\tau = 5 \times 10^{-4}$; (b) the value of $F_{\exp}$ is $F_{\exp} = 0.35$ kg/m$^3$ for the data related to [11]; (c) the value of $F_{\exp}$ is $F_{\exp} = 1.45$ kg/m$^3$ for the data related to [12]; (d) the value of $F$ is $F = 1.30$ kg/m$^3$ for the data related to equation (8).

Fourthly, a good agreement between the function $F_{\text{opt}}$ and the function $F_{\exp}$ allows us to assume that the diameter $f_{\text{dopt}}$ has a following form

$$f_{\text{dopt}} = B_{d0}\tau^{1-\alpha_4} + B_{d_{\exp}}\tau^{2\beta_4},$$

where $B_{d0}$ and $B_{d_{\exp}}$ are the coefficients found on a basis of experimental data on the density at the saturation line.

It is considered one more variant of $F_{\beta_{\exp}}$ in the form $F_{\beta_{\exp}} = -B_{d_{\exp}}\tau^{2\beta_4}\rho_c$ and the following conditions:

$$F_{\text{opt}} = -B_{d_{\exp}}\tau^{2\beta_4}\rho_c + B_{d0}\tau^{1-\alpha_4}\rho_c,$$

where $F_{\text{opt}}$ is located between $F_{\exp}$ and the boundary, $F_{\text{low}} = F_{\exp} - \Delta \rho$.

It can be written $F_{\beta_{\exp}} = -F_{\alpha}$ and $F_{\text{opt}} = 0$ at $\tau_A = 3 \times 10^{-5}$. There is some anomaly region, $0 < \tau < \tau_A$, where $F_{\text{opt}} < 0$,

$$df_d/d\tau \approx -B_{d_{\exp}}\tau^{2\beta_4-1} \rightarrow -\infty \text{ for } \tau \rightarrow 0;$$

compare relation (33) with condition (iv). Our evaluation has shown:
(i) starting \((\rho_g, \rho_l, T)\)-points [10], which are used in the work [5], have a considerably higher error (about an order of the magnitude) than the estimate of \(\delta \rho_{\text{exp}}\) related to \((\rho_g, \rho_l, T)\)-data [12],

(ii) the value of \(f_{\text{exp}}\), which are derived from \((\rho_g, \rho_l, T)\)-points [12], deviate systematically from the values of \(f_{\text{exp}}\) related to \((\rho_g, \rho_l, T)\)-data [10]; this cause leads to a low accuracy of \(f_{\text{opt}}\) related to model (8).

4. Conclusion

The proposed method gave the possibility to obtain the equation for the diameter, \(f_{\text{exp}}\), which contains a term \(B_{\text{exp}} \tau^{2\beta_4}\). For example, our test with SF\(_6\) has given numerical estimates of the parameters \(\alpha_4\) and \(\beta_4\) using statistical treaty of experimental \((\rho_g, \rho_l, T)\)-data [12] in contrast to \(\alpha\) and \(\beta\) those are related to equation (8) and chosen as theoretical values.

Our analysis has shown that the equation \(f_{\text{exp}}\) (31) coincides with the experimental values of \(f_{\text{exp}}\) within the limits caused by the error of the reference data at temperatures \(\tau = \tau_{\text{low}} \cdots 0.01\). A comparison of equations (31), (4) and (8) shows:

(i) the coefficient \(B_{\text{opt}}\) coincides in the sign with the coefficient \(B_{\text{opt}}\) of equation (8), parameters \((\alpha_4, \beta_4)\) coincide with the same parameters \((\alpha_1, \beta_1)\) within \((1 \cdots 3)\%\);

(ii) the coefficient \(B_{\text{opt}}\) of equation (31) is positive, and the coefficient \(B_{\text{opt}}\) of equation (8) is negative, which contradicts the hypothesis, \(H_{\text{ML}}\).

Equation (31) provides an important condition, which is typical for equations (8) and (28), namely, the derivative \(df_{\text{opt}}/d\tau\) is singular \((df_{\text{opt}}/d\tau \approx B_{\text{opt}} \tau^{2\beta_4-1}\) when \(\tau \to 0\). The numerical data on the equation (31) explain the fact that the rate of \((1 - \alpha_4)\) lies in the range of 0.85 \cdots 0.90 and is found by processing the experimental \((\rho_g, \rho_l, T)\)-data for a large number of substances. These values significantly exceed the degree included of \(2\beta_4 = 0.65\), which is the equation of diameter \(f_2(9)\).

Due to our oppenion, \(f_2\) has the form \(f_2 \approx B_{\text{opt}} \tau^{2\beta_4} > B_{\text{opt}} \tau^{1-\alpha_4}\) at \(\tau < \tau_A\); it will be possible to determine the term, \(B_{\text{opt}} \tau^{2\beta_4}\), more accurately on the basis of experimental data to be obtained for the SF\(_6\) at temperatures \(0 < \tau < 0.00003\).

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References

[1] Wegner C 1985 Int. J. Thermophys. 11 421
[2] Anisimov M A et al 1990 Termodinamika Kriticheskogo Sostoyaniya Individual'nykh Veshchestv (Moscow: Energizdat)
[3] Landau L and Lifshitz M 1964 Statisticheskaya Fizika (Moscow: Fizmatizd)
[4] Ustjuzhanin E E, Reutov B F, Utenkov V F and Rykov V A 2007 Soft Matter under Exogenic Impact. NATO Science Series II vol 242 ed Rzoska S and Mazur V (Springer) p 325
[5] Anisimov M A and Wang J 2007 Phys. Rev. E 75 051107
[6] Apfelbaum E M and Vorobyev V S 2015 J. Phys. Chem. B 119 8419
[7] Kim Y C, Fisher M E and Orkoulas G 2003 Phys. Rev. E 67 061506
[8] Ustjuzhanin E E, Shishakov V V, Popov P V, Rykov V A and Frenkel' M L 2011 Vestnik MEI 6 167
[9] Rabinovich V A and Shehudyak Y E 1995 Teplot fiz. Vys. Temp. 33 546
[10] Rykov V A, Rykov S V and Ustjuzhanin E E 2015 Scientific and Technical Volga Region Bulletin 6 27
[11] Funke M, Kleinrahm R and Wagner W 2001 J. Chem. Thermodyn. 34 735
[12] Weiner J, Langley K H and Ford N C 1974 Phys. Rev. Lett. 32 879