

Comparison of the scaling models for substance densities along saturation line

V S Vorob'yev¹, V A Rykov², E E Ustyuzhanin³, V V Shishakov³,
P V Popov³ and S V Rykov²

¹ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia

² ITMO University, Kronvergskiy 49, Saint-Petersburg 197101, Russia

³ National Research University Moscow Power Engineering Institute, Krasnokazarmennaya 14, Moscow 111250, Russia

E-mail: evgust@gmail.com

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 T_c . 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 (ρ_l), the gas density (ρ_g) of the order parameter (f_s), the mean diameter (f_d) etc) in a specified neighborhood of the critical temperature T_c . 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 (C_v).

Our analysis shows that the different values of the critical exponent $\alpha = (\alpha_1, \alpha_2, \dots)$ used in the literature. For example, in common prior to 2000 scaling model of Wegner [1] uses the following series

$$f_s = (\rho_l - \rho_g) (2\rho_c)^{-1} = B_{s0}\tau^{\beta_1} + B_{s1}\tau^{\beta_1+\Delta}, \quad (1)$$

$$f_d = (\rho_l + \rho_g) (2\rho_c)^{-1} - 1 = B_{d0}\tau^{1-\alpha_1} + B_{d1}\tau^{1-\alpha_1+\Delta} + B_{d2}\tau, \quad (2)$$



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_{si} , B_{di})—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 df_d/dT is singular ($df_d/dT \approx B_{d0}\tau^{1-\alpha_1} \rightarrow -\infty$ when $\tau \rightarrow 0$, the parameter α_1 is small). Earlier, the first theoretical step in the construction of the functions ($\rho_g, \rho_l, f_s, f_d \dots$) 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 ($\Delta\rho = \rho/\rho_c - 1$), τ). 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 α_2 and β_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} , ρ_c , T_c , β_2 , α_2), while β_2 and α_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

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

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

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} , ρ_c , T_c , β_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 β_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} , ρ_c , T_c , β , α) are placed for a wide range of substances. So, in 1990 Anisimov [2] has developed a model that includes α_1 and β_1 , proposed by Wegner [1]. His model has a satisfactory accuracy in the interval $\tau_{\text{low}} \dots \tau_{\text{high}} = 10^{-4} \dots 10^{-2}$ for H_2O and is written in the form

$$f_s = B_{s0}\tau^{\beta_1} + B_{s1}\tau^{\beta_1+\Delta}, \quad (6)$$

$$f_d = B_{d0}\tau^{1-\alpha_1} + B_{d1}\tau, \quad (7)$$

where B_{si} , B_{di} —coefficients determined by statistical processing of experimental data on the densities of H_2O .

A new hypothesis (H_A) connects the diameter, f_d , with the chemical potential, μ , 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

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

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 α_1 and β_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 α_1 and β_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

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

The derivative df_d/dT is singular ($df_d/dT \approx \tau^{2\beta_1-1}$ for $\tau \rightarrow 0$) for equations (8) and (9). Equations (9) and (4) are similar in the shape: the exponent β_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 SF₆ and N₂ in the range $\tau_{\text{low}} \cdots \tau_{\text{high}} = 10^{-4} \cdots 10^{-2}$. At the same time in their calculations, the authors of [5] attracted the experimental data on such properties along the saturation line as density ρ , 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 (α_{exp} , β_{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 α and β mentioned above. The values of α_{exp} are given in references [2, 4, 8, 9] and cover a whole range $\alpha_{\text{exp}} = 0.10 \cdots 0.14$.

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

Fourthly, a wide range of values of α and β , 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 (α , β , 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 μ_g , μ_l on the saturation line in the form

$$(d\mu_l/dT) = v_l (dP/dT) - s_l, \quad (10)$$

$$(d\mu_g/dT) = v_g (dP/dT) - s_g, \quad (11)$$

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

$$d\mu_g/dT + d\mu_l/dT = (v_g + v_l) (dP/dT) - (s_g + s_l). \quad (12)$$

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

$$v_g + v_l = (\rho_g + \rho_l)/(\rho_g \rho_l). \quad (13)$$

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

$$\begin{aligned} \rho_g + \rho_l &= (v_g + v_l)(\rho_g \rho_l) = \\ &= (d\mu_g/dT + d\mu_l/dT + s_g + s_l) (dP/dT)^{-1} (\rho_g \rho_l). \end{aligned} \quad (14)$$

The third step will present the components of equation (14) those are the leading members of the scaling at small τ . For example, the terms, $B_{s0}\tau^\beta$, $B_{d0}\tau^{1-\alpha}$, 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

$$dP/dT = B_{p1} (1 - B_{p0}\tau^{1-\alpha} + o(\tau)) \approx B_{p1} (1 - B_{p0}\tau^{1-\alpha}), \quad (15)$$

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

$$d\mu_g/dT = B_{M1g} (1 - B_{M0g}\tau^{1-\alpha} + o(\tau)) \approx B_{M1g} (1 - B_{M0g}\tau^{1-\alpha}), \quad (16)$$

where $(d\mu_g/dT)_c = B_{M1g}$, $d^2\mu_g/dT^2 = B_{C1g}C_{v_g}(\tau) = B_{C2g}\tau^{-\alpha}$,

$$d\mu_l/dT = B_{M1l} (1 - B_{M0l}\tau^{1-\alpha} + o(\tau)) \approx B_{M1l} (1 - B_{M0l}\tau^{1-\alpha}), \quad (17)$$

where $(d\mu_l/dT)_c = B_{M1l}$, $d^2\mu_l/dT^2 = B_{C1l}C_{v_l}(\tau) = B_{C2l}\tau^{-\alpha}$,

$$s_g = B_{Sg}\tau^{1-\alpha}v_g + A_{s1} + A_{s2}\tau + (B_1 + B_2\tau)v_g + o(\tau), \quad (18)$$

$$s_l = B_{Sl}\tau^{1-\alpha}v_l + A_{s1} + A_{s2}\tau + (B_1 + B_2\tau)v_l + o(\tau). \quad (19)$$

The connection between the chemical potential and the specific heat has the form, $d^2\mu_g/dT^2 = B_{C1g}C_{v_g}(\tau) = B_{C2g}\tau^{-\alpha}$, 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

$$\begin{aligned} \rho_g \rho_l &= \rho_c^2 (1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta} + \dots) \approx \\ &\approx \rho_c^2 (1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta}). \end{aligned} \quad (20)$$

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

$$\begin{aligned} v_l &= 1/\rho_l = 1/(\rho_c (1 + \Delta\rho_l)) = 1/\rho_c (1 - \Delta\rho_l + \Delta\rho_l^2 + \dots) \approx \\ &\approx 1/\rho_c (1 - B_{s0}\tau^\beta - B_{d0}\tau^{1-\alpha} + B_{s0}^2\tau^{2\beta}), \end{aligned}$$

$$v_g = 1/\rho_g = 1/(\rho_c(1 + \Delta\rho_g)) = 1/\rho_c (1 - \Delta\rho_g + \Delta\rho_g^2 + \dots) \approx \quad (21)$$

$$\approx 1/\rho_c (1 + B_{s0}\tau^\beta - B_{d0}\tau^{1-\alpha} + B_{s0}^2\tau^{2\beta}),$$

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

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

$$\begin{aligned} d\mu_g/dT (dP/dT)^{-1} (\rho_g\rho_l) &= \\ &= B_{M1g} (1 - B_{M0g}\tau^{1-\alpha}) B_{p1}^{-1} (1 + B_{p0}\tau^{1-\alpha}) \rho_c^2 (1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta}) = \\ &= A_{Mg} (1 + B_{p0}\tau^{1-\alpha} - B_{M0g}\tau^{1-\alpha} + \dots) (1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta}) = \\ &= A_{Mg} (1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta} + B_{p0}\tau^{1-\alpha} + \dots), \end{aligned}$$

where $A_{Mg} = B_{M1g}B_{p1}^{-1}\rho_c^2$,

$$\begin{aligned} d\mu_l/dT (dP/dT)^{-1} (\rho_g\rho_l) &= \\ &= B_{M1l} (1 - B_{M0l}\tau^{1-\alpha}) B_{p1}^{-1} (1 + B_{p0}\tau^{1-\alpha}) \rho_c^2 (1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta}) = \\ &= A_{Ml} (1 + B_{p0}\tau^{1-\alpha} - B_{M0l}\tau^{1-\alpha} + \dots) (1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta}) = \\ &= A_{Ml} (1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta} + B_{p0}\tau^{1-\alpha} + \dots), \end{aligned} \quad (22)$$

where $A_{Ml} = B_{M1l}B_{p1}^{-1}\rho_c^2$.

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

$$\begin{aligned} s_g(dP/dT)^{-1}(\rho_g\rho_l) &= B_{Sg}\tau^{1-\alpha}B_{p1}^{-1}(1 + B_{p0}\tau^{1-\alpha})\rho_l + \\ &+ (A_{s1} + A_{s2}\tau)B_{p1}^{-1}(1 + B_{p0}\tau^{1-\alpha})\rho_c^2(1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta}) + \\ &+ (B_1 + B_2\tau)B_{p1}^{-1}(1 + B_{p0}\tau^{1-\alpha})\rho_l = \\ &= A_{s1}B_{p1}^{-1}\rho_c^2 + B_1B_{p1}^{-1}\rho_c - A_{s1}B_{p1}^{-1}\rho_c^2B_{s0}^2\tau^{2\beta} + \dots, \\ s_l(dP/dT)^{-1}(\rho_g\rho_l) &= B_{Sl}\tau^{1-\alpha}B_{p1}^{-1}(1 + B_{p0}\tau^{1-\alpha})\rho_l + \\ &+ (A_{s1} + A_{s2}\tau)B_{p1}^{-1}(1 + B_{p0}\tau^{1-\alpha})\rho_c^2(1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta}) + \\ &+ (B_1 + B_2\tau)B_{p1}^{-1}(1 + B_{p0}\tau^{1-\alpha})\rho_l = \\ &= A_{s1}B_{p1}^{-1}\rho_c^2 + B_1B_{p1}^{-1}\rho_c - A_{s1}B_{p1}^{-1}\rho_c^2B_{s0}^2\tau^{2\beta} + \dots. \end{aligned} \quad (23)$$

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

$$\begin{aligned} \rho_g + \rho_l &= A_{Mg} (1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta} + B_{p0}\tau^{1-\alpha} + \dots) + \\ &+ A_{Ml} (1 + 2B_{d0}\tau^{1-\alpha} - B_{s0}^2\tau^{2\beta} + B_{p0}\tau^{1-\alpha} + \dots) + \\ &+ 2(A_{s1}B_{p1}^{-1}\rho_c^2 + B_1B_{p1}^{-1}\rho_c - A_{s1}B_{p1}^{-1}\rho_c^2B_{s0}^2\tau^{2\beta}) + \dots, \end{aligned} \quad (24)$$

where the coefficients and parameters are related by the equation

$$2\rho_c = A_{Mg} + A_{Ml} + 2(A_{s1}B_{p1}^{-1}\rho_c^2 + B_1B_{p1}^{-1}\rho_c). \quad (25)$$

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

ρ_c , kg/m ³	T_c , K	α_4	β_4	B_{s0}	B_{s1}	B_{s2}
742.255	318.709	0.1099	0.3474	1.9575	-0.024777	0.142317
B_{s3}	B_{s4}	B_{d0}	B_{d1}	B_{d2}	B_{d3}	B_{d4}
-1.324779	1.60129	0.4695	0.597385	0.85706	-1.250538	0.334847

We write amount $(\rho_g + \rho_l)$, allocating first member comprising $\tau^{2\beta}$ function in the form

$$\begin{aligned} \rho_g + \rho_l &= 2\rho_c + 2A_{M_g}B_{d0}\tau^{1-\alpha} - A_{M_g}B_{s0}^2\tau^{2\beta} - \\ &- A_{M_l}B_{s0}^2\tau^{2\beta} - 2A_{s1}B_{p1}^{-1}\rho_c^2B_{s0}^2\tau^{2\beta} + \dots = \\ &= 2\rho_c + A_{d0}\rho_c\tau^{1-\alpha} + 2A_{d2}\rho_c\tau^{2\beta} + \dots \end{aligned} \quad (26)$$

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

$$f_d = A_{d0}\tau^{1-\alpha} + A_{d2}\tau^{2\beta} + \dots \quad (27)$$

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 $(\rho_l, \rho_g, f_s, f_d)$ for sulphur hexafluoride, which is selected as a test substance with very precise experimental (ρ_g, ρ_l, 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_{scale}) and regular (F_{reg}) parts with the numerical parameters in relation to SF₆. These equations have a form

$$f_s = B_{s0}\tau^{\beta_4} + B_{s1}\tau^{\beta_4+\Delta} + B_{s2}\tau^{\beta_4+2\Delta} + B_{s3}\tau^2 + B_{s4}\tau^3, \quad (28)$$

$$f_d = B_{d0}\tau^{1-\alpha_4} + B_{d1}\tau^{1-\alpha_4+\Delta} + B_{d2}\tau^{1-\alpha_4+2\Delta} + B_{d3}\tau^2 + B_{d4}\tau^3, \quad (29)$$

where $B_{si}, B_{di}, i = 0, 1, 2$ -coefficients related to F_{scale} , $B_{si}, B_{di}, i = 3, 4$ -coefficients related to F_{reg} , α_4, β_4 -indices defined on the basis of statistical treatment of experimental (ρ_g, ρ_l, T) -data.

F_{scale} structure meets MT. Equations (28) and (29) include the optimal values of the critical parameters $(T_c, \rho_c, \alpha_4, \beta_4, B_{s0}, B_{d0})$, which are calculated with empirical coefficients (B_{si}, B_{di}) on the basis of experimental (ρ_g, ρ_l, 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_{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 (ρ_g, ρ_l, T) -data [11] of SF₆. Parameters $(T_c, \rho_c, \alpha_4, \beta_4, B_{s0}, B_{d0})$ is used as an initial approximation parameters of equation (27).

In accordance with NLLSM an initial approximation for the parameters $(T_c, \rho_c, \alpha_4, \beta_4, B_{s0}, B_{d0})$ was chosen in accordance with literature data including 1) $\alpha_4 = 1 - 2\beta_1 = 0.35$ in accordance with the hypothesis H_A , 2) $\beta_4 = 0.325$. The proposed equations reproduce the most

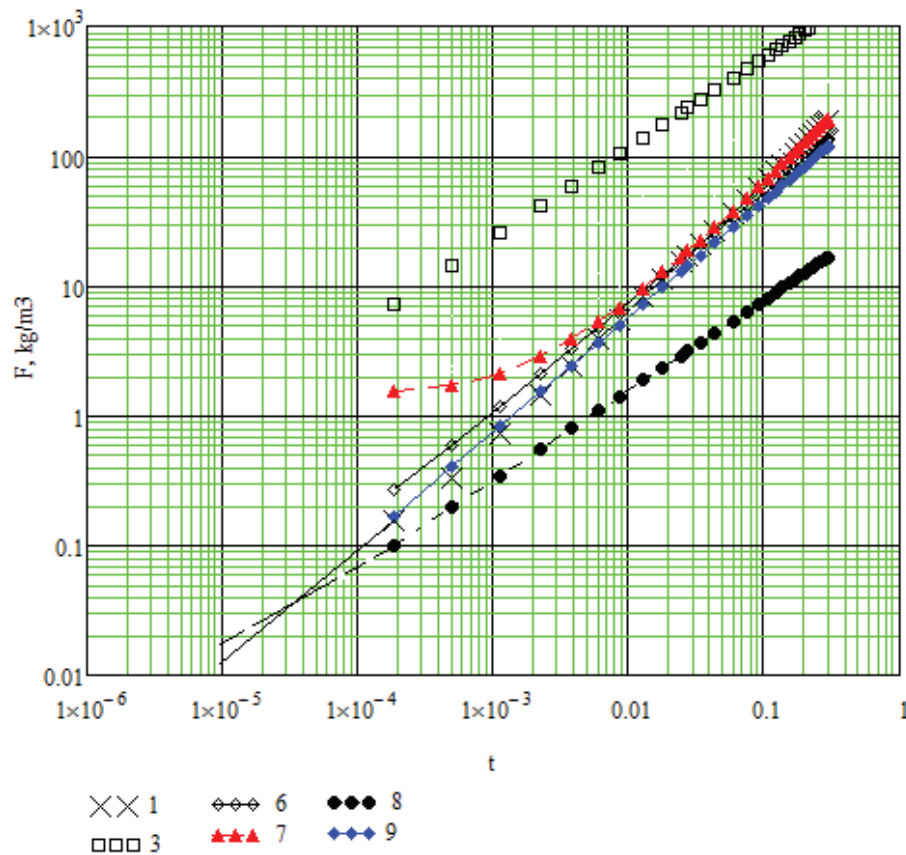


Figure 1. An additional function F and its members. 1—function F_{exp} , built from experimental (ρ_g, ρ_l, T) -data [11], 3—term $B_{s0}^2 \tau^{2\beta_4} \rho_c$, 6—sum of terms $B_{d\text{exp}} \tau^{2\beta_4} \rho_c + B_{d0} \tau^{1-\alpha_4} \rho_c$; 7—limit F_{high} , 8—term $B_{d\text{exp}} \tau^{2\beta_4} \rho_c$, 9—term $B_{d0} \tau^{1-\alpha_4} \rho_c$.

accurate (ρ_g, ρ_l, T) -data [11], covering the interval from τ_{low} to τ_{tr} with 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).

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

$$F = (\rho_g + \rho_l)/2 - \rho_c = \rho_c f_d = F_\alpha + F_\beta + \dots, \quad (30)$$

where F_α and F_β —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_{exp} (symbols 1, figure 1) calculated on the base of experimental (ρ_g, ρ_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_{exp} lies in the range $\Delta\rho = \pm 1.4 \text{ kg/m}^3$ at $\tau = \tau_{\text{low}} \dots 0.3$. We have got F that coordinates satisfactory (within the estimate of δF_{exp}) to equation (29) and to the values of F_{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),

- (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, $B_{s0}^2\tau^{2\beta}\rho_c$, (symbols 3), which includes the coefficient B_{s0} (table 1) follows to recommendations [5].

It possible to conclude from our comparison:

- (i) the term F_α coinsides with the function F_{exp} at $\tau = \tau_{\text{low}} \cdots 0.01$,
- (ii) the term, $B_{s0}^2\tau^{2\beta}\rho_c$, is substantially higher than the function F_{exp} at $\tau = \tau_{\text{low}} \cdots 0.3$,
- (iii) the term, $B_{s0}^2\tau^{2\beta}$, 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 $f_{d_{\text{exp}}}$.

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

- (i) $B_{d_{\text{exp}}} = 0.0518$,
- (ii) sum $B_{d_{\text{exp}}}\tau^{2\beta_4}\rho_c + B_{d0}\tau^{1-\alpha_4}\rho_c$ represents the function F_{opt} (symbol 6); it locates between the function F_{exp} and the limit F_{high} ,
- (iii) the term $F_{\beta_{\text{exp}}}$ (symbols 8) intersects the term F_α (symbols 9) when $\tau = 3 \times 10^{-5}$; the term $F_{\beta_{\text{exp}}}$ is a liding term compared to term F_α at smaller τ ; it is possible to accept that there is a temperature limit $\tau_A = 3 \times 10^{-5}$; f_d has the form $f_d \approx B_{d_{\text{exp}}}\tau^{2\beta_4} > B_{d0}\tau^{1-\alpha_4}$ at $\tau < \tau_A$.
- (iv) $df_d/d\tau \approx B_{d_{\text{exp}}}\tau^{2\beta_4-1} \rightarrow \infty$ for $\tau \rightarrow 0$.

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

Thirdly, the comparison of the equations let us conclude: (a) the function F_{exp} ((ρ_g, ρ_l, T) -points [12]) located systematically higher than the function F_{exp} ((ρ_g, ρ_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 $F_{\text{exp}} = 0.35 \text{ kg/m}^3$ for the data related to [11]; (c) the value of F_{exp} is $F_{\text{exp}} = 1.45 \text{ kg/m}^3$ for the data related to [12]; (d) the value of F is $F = 1.30 \text{ kg/m}^3$ for the data related to equation (8).

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

$$f_{d_{\text{opt}}} = B_{d0}\tau^{1-\alpha_4} + B_{d_{\text{exp}}}\tau^{2\beta_4}, \quad (31)$$

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

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

$$F_{\text{opt}} = -B_{d_{\text{exp}}}\tau^{2\beta_4}\rho_c + B_{d0}\tau^{1-\alpha_4}\rho_c, \quad (32)$$

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

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

$$df_d/d\tau \approx -B_{d_{\text{exp}}}\tau^{2\beta_4-1} \rightarrow -\infty \text{ for } \tau \rightarrow 0; \quad (33)$$

compare relation (33) with condition (iv). Our evaluation has shown:

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

4. Conclusion

The proposed method gave the possibility to obtain the equation for the diameter, $f_{d_{\text{opt}}}$, which contains a term $B_{d_{\text{exp}}}\tau^{2\beta_4}$. For example, our test with SF_6 has given numerical estimates of the parameters α_4 and β_4 using statistical treaty of experimental (ρ_g, ρ_l, T) -data [12] in contrast to α and β those are related to equation (8) and chosen as theoretical values.

Our analysis has shown that the equation $f_{d_{\text{opt}}}$ (31) coincides with the experimental values of $f_{d_{\text{exp}}}$ 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 $B_{d_{\text{opt}}}$ coincides in the sign with the coefficient B_{d2} of equation (8), parameters (α_4, β_4) coincide with the same parameters (α_1, β_1) within $(1 \cdots 3)\%$;
- (ii) the coefficient B_{d0} of equation (31) is positive, and the coefficient B_{d0} of equation (8) is negative, which contradicts the hypothesis, H_{ML} .

Equation (31) provides an important condition, which is typical for equations (8) and (28), namely, the derivative $df_d/d\tau$ is singular ($df_d/d\tau \approx B_{d_{\text{exp}}}\tau^{2\beta_4-1}$ when $\tau \rightarrow 0$). The numerical data on the equation (31) explain the fact that the rate of $2\beta_1 \approx 0.65$ has not been calculated in any of the works in which the indexes of f_d are defined on the basis of processing the experimental (ρ_g, ρ_l, T) -data. Our analysis shows that the term $B_{d_{\text{exp}}}\tau^{2\beta_4}$ is small in comparison with the term $B_{d0}\tau^{1-\alpha_4}$ at temperatures $\tau_{\text{low}} \cdots 0.01$. Therefore the diameter, f_d , contains a term, $B_{d0}\tau^{1-\alpha_4}$ in the known equations; the degree, $(1 - \alpha_4)$ lies in the range of $0.85 \cdots 0.90$ and is found by processing the experimental (ρ_g, ρ_l, T) -data for a large number of substances. These values significantly exceed the degree included of $2\beta_1 = 0.65$, which is the equation of diameter $f_d(9)$. Due to our opinion, f_d has the form $f_d \approx B_{d_{\text{exp}}}\tau^{2\beta_4} > B_{d0}\tau^{1-\alpha_4}$ at $\tau < \tau_A$; it will be possible to determine the term, $B_{d_{\text{exp}}}\tau^{2\beta_4}$, 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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