The method for constructing the fundamental equation of state for SF$_6$

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Abstract. The paper investigates issues related to construction of the equation of state which takes into account the peculiarities of substance behavior in the critical region and which is associated with the scalihg theory of critical phenomena. Construction method of a unified fundamental equation of state (UF EOS) for SF$_6$ that satisfies the power laws of scaling theory (ST) and the requirements imposed on the fundamental equations of state of the virial form (F EOS) is considered. UF EOS is based on a new representation of the scaling hypothesis in variables density – temperature and Benedek hypothesis. The authors have developed F EOS for SF$_6$ in the range of state parameters: in density up to 2000 kg/m$^3$, in temperature from 223.555 to 650 K. The authors have performed comparison with the certain fundamental equations of state for SF$_6$: Scalabrin et al (2007 J. Phys. Chem. Ref. Data 36 617), Guder et al (2009 J. Phys. Chem. Ref. Data 38 33); Bezverkhii (2017 High Temp. 55 702). It is shown that in accordance with the requirements of ST, in contrast to the certain F EOS, the proposed equation of state transmits SF$_6$ behavior into the vicinity of the critical point and in this region of state parameters significantly exceeds them in accuracy.

1. Introduction
The problem of constructing the fundamental equation of state (FEOS) which takes into account the behavior of a substance in the region of critical states attracts the attention of many researchers [1–10]. One can mention several approaches that have been most successful.

The authors of works [1–3] have developed crossover equations of state, which are written in parametric form and are transferred to the equation of state of Schofield–Litster–Ho (LM) [11] in the asymptotic vicinity of the critical point.

In works [4,5], when constructing crossover equations of state, Landau decomposition [12] in density-temperature variables ($\rho,T$) is used. Our analysis of works [1–5] shows that crossover equations [1–5] have a workspace which is limited by the following parameters: $0.6 \leq \omega \leq 2.0$ and $0.96 \leq t \leq 1.2$ ($\omega = \rho/\rho_c$, $t = T/T_c$).

The authors of [6] proposed to solve the problem of constructing FEOS for SF$_6$ on the basis of a combined equation for pressure having an empirical form. This equation includes the following components:

- a function $p_{reg}(\rho,T) = [1-Y(\rho,T)]p_r(\rho,T)$, which includes a regular function $p_r(\rho,T)$, and a crossover function $Y(\rho,T)$:

$$Y = \omega(1 - \omega/\omega_t)^2/(1 - \omega/\omega_t)^2 e r f c \left( \sqrt{\lambda/\tau} \right) \exp (-\mu \Delta \rho^2)$$; (1)
• an irregular function \( p_{\text{scal}}(\rho, T) \), which is calculated on the basis of a nonparametric equation of the scaling form.

Here \( \omega_t = \rho/\rho_t \); \( \rho_t \) is the vapor density at the triple point.

Note that a scaling function of a chemical potential \( \mu(x) \) used in [6] can be strictly calculated [13] at the values of critical indices \( \delta = 5 \) and \( \gamma = 4\beta \) on the basis of the phenomenological theory of Migdal critical point [14] and Benedek hypothesis [15].

In order to convey qualitatively right the behavior of the critical isotherm and isothermal compressibility coefficient \( K_T \), the following relationships for derivatives should be fulfilled [16]:

\[
(\partial^n p/\partial \rho^n)\big|_{T=T_c, \rho=\rho_c} = 0, \quad (\partial p/\partial \rho)\big|_{\rho=\rho_c, T=\tau} \sim o(\tau),
\]

where \( n \in \{1, 2, 3, 4\} \), \( \rho_c \) and \( T_c \) are critical parameters, \( o \) is Landau symbol.

Within the approach [6], only three equalities from conditions (2) are satisfied, namely, with \( n \in \{1, 2, 3\} \). This leads to the fact that the critical isotherm in the asymptotic vicinity of the critical point is described by the equation \( \Delta p = A_0|\Delta \rho|^2 \), where \( A_0 = \text{const} \neq 0 \). That is, the critical index \( \delta \) of the critical isotherm is equal to \( \delta = 3 \), and not \( \delta = 4.815 \) which is used by the authors of [6] in accordance with Ising model. In addition, the computational formulas [6] for Helmholtz free energy \( F \), entropy \( s \), enthalpy \( i \), sound velocity \( w \), isochoric \( C_V \) and isobaric \( C_p \) heat capacity include integrals of differential binomials and functions \( Y(1) \).

To construct the fundamental equation of state, the authors of [7–10] used Helmholtz free energy \( F(\rho, T) \) and the method of pseudocritical points [17] which position on the thermodynamic surface is determined by the equalities [18]: \((\partial \rho/\partial T)_{\rho} = 0 \) and \((\partial T/\partial s)_{\rho} = 0 \).

Meanwhile, the authors of [7–10] chose the structure \( F(\rho, T) \) in such a way as to satisfy the power laws of the scaling theory (ST). Using the example of argon and R134a in [8,9], it is shown that the working region of this equation of state is not inferior to the range of state parameters in which the FEOs considered in [19,20] work satisfactorily. Note that the equation of state proposed in [7–9] has an empirical form as well as the equation of state in [6].

This paper is devoted to the development of a unified fundamental equation of state (UFEoS) for SF6. Meanwhile, in accordance with [21], we understand the unified equation of state as a single-structure form \( F(\rho, T) \) which transfers the equilibrium properties of liquid and gas in the single-phase region, on the phase equilibrium line from the triple point to the critical point, including the critical point vicinity and metastable states with small uncertainty.

### 2. The structure of UFEoS obtained on the basis of a new presentation of the scaling hypothesis

The proposed method of constructing UFEoS is based on the presentation of a scaling hypothesis in the following form [22]:

\[
\Delta S X^{-\frac{1-n}{\alpha}} = \varphi_0 + \varphi_2 \rho^2, \quad m = \Delta \rho X^{\frac{\alpha}{2}}, \tag{3}
\]

where \( \Delta S = (\rho T_c/p_c)[S(\rho, T) - S_0(\rho, T)]/\phi_0(\omega) \); \( S_0(\rho, T) \) and \( \phi_0(\omega) \) are regular functions; \( p_c \) is the critical pressure; \( \Delta \rho = \omega - 1; \alpha, \beta, \chi \) are critical indices; \( X_1 \) is the thermodynamic function, which is characterized by a critical index \( \chi \) (for example, \( X = X_1 = C_v \) and \( \chi = \chi_1 = \alpha, X = X_2 = K_T \) and \( \chi = \chi_2 = \gamma \)).

In paper [23], it is shown that on the basis of (3) by means of a certain thermodynamic relation \( F = - \int s \, dT \) and the superposition principle, one can construct a fundamental equation of state in the form:

\[
F(\rho, T) = F_{\text{reg}}(\rho, T) + F_{\text{irreg}}(\rho, T), \tag{4}
\]

where \( F_{\text{reg}}(\rho, T) \) is a regular function; \( F_{\text{irreg}}(\rho, T) \) is an irregular component of Helmholtz free energy:

\[
F_{\text{irreg}}(\rho, T) = p_c \phi_0(\omega)|\Delta \rho|^{\delta+1}a(x). \tag{5}
\]
Here $\delta$ is a critical index of the critical isotherm; $a(x)$ is the scaling function of Helmholtz free energy.

In this paper, a function $a(x)$ [23] is used:

$$a(x) = A_1(x + x_1)^{2-\alpha} + A_2(x + x_2)^{2-\alpha} + B_3(x + x_3)^2 + C,$$  \hfill (6)

where $x = \tau/\Delta\rho^{1/\beta}$; $\tau = t - 1$; $A_2 = -\varepsilon A_1$, $A_1 = -(u_0k\gamma_1)/(2\alpha b\alpha_1(1 - \varepsilon))$, $B_1 = u_0/(2k)$, $u_0$ is the individual constant of the substance, $\alpha_1 = (2 - \alpha)(1 - \alpha)$, $\gamma_1 = \gamma(\gamma - 1)$, $\varepsilon = x_1/x_2$, $x_i = \varphi_i x_0$, $i \in \{1, 2, 3\}$, $k = (b^2 - 1)^{\beta}/x_0^\beta$, $b^2 = (\gamma - 2\beta)/[\gamma(1 - 2\beta)]$, $\varphi_1 = 2.824299$, $\varphi_2 = 14.68239975$, $\varphi_3 = 5.78070021$, $x_0$ is the individual parameter of the substance; $C$ is the constant which we find in the equality: $(2 - \alpha)a(x = -x_0) - x\alpha'(x = -x_0) = 0$.

Note that function (6) is designed on the basis of Benedek hypothesis [15].

Deviations of scaling functions $h(x)$ and a scaling function of the isothermal compressibility coefficient $f_z(x) = (\delta h(x) - x/\beta h'(x))^{-1}$ calculated on the basis of a scaling function (6) from the corresponding scaling functions of LM [11] do not exceed 1% [24]. Thus, a scaling function (6) is not inferior to LM in its design characteristics and can be recommended for calculating singular components of wide-range equations of state.

3. Selection of a crossover function and a regular component of UFfEoS

A regular component of free energy $F_{\text{reg}}(\rho, T)$ and a function $\phi_0(\omega)$ should be selected on the basis of the following considerations. Firstly, in the region of rarefied gas, a thermal equation of state calculated on the basis of (4) should be converted to an equation of state of the virial form:

$$Z(\rho, T) = 1 + \omega B(\rho) + \omega^2 C(\rho) + \ldots,$$

where $Z(\rho, T) = p/(\rho RT)$; $R$ is the gas constant; $B(T)$ and $C(T)$ are the second and third virial coefficients, respectively.

Secondly, in the critical point vicinity, equation (4) should be converted to Widom equation [25]:

$$\Delta\mu = \Delta\rho|\Delta\rho|^{\delta-1}h(x).$$  \hfill (8)

Select a function $F_{\text{reg}}(\rho, T)$ in the form:

$$F_{\text{reg}}(\rho, T) = RT\ln(\omega) + RT\sum_{i=0}^{1} \sum_{j=0}^{n_2} C_{i,j}\tau_i^j(\Delta\rho)^i,$$

where $C_{i,j}$ are constant coefficients; $\tau_1 = T_c/T - 1$.

Considering the requirements (2) we will bring FEoS (4), (9) to the following form:

$$F(\rho, T) = RTF^{(\text{id})}(T, \rho) + RT\omega y_2 + RT\omega (Z_c - 0.2)y_6 + RT\omega \tau_1 [D_1(\omega - 3) + D_2(\omega^2 - 2\omega)] + RT\omega D_3(y_4 - y_6)$$

$$+ RT\omega \sum_{i=0}^{22} \sum_{j=0}^{6} (C_{i,j}\tau_i^j(\Delta\rho)^i) + RT\omega \phi_0(\omega)|\Delta\rho|^{\delta+1}a(x),$$  \hfill (10)

where $F^{(\text{id})}(T, \rho)$ is the ideal-gas component of free energy; $y_2 = -7.76 + 2.9/6\Delta\rho - 1.1/6\Delta\rho^2 + 0.05\Delta\rho^3$; $y_4 = 5 - 4\Delta\rho + 3\Delta\rho^2 - 2\Delta\rho^3 + \Delta\rho^4$; $y_6 = 4 - 3\Delta\rho + 2\Delta\rho^2 - \Delta\rho^3 + \Delta\rho^5$; $Z_c = p_c/(\rho_c T_c) \times 10^6$.

We have considered various versions of crossover functions used in works [10, 24, 29, 30].

As a result, we have utilized the function $\phi_0$ used in works [10, 29]:

$$\phi_0(\omega) = \left[(\Delta\rho)^2 - 1\right]^2.$$  \hfill (11)

UFfEoS (10) with a crossover function (11) satisfies:
• the requirements usually imposed on equations of state of the virial form [21];
• power laws of a scaling hypothesis describing the behavior of thermodynamic surface in the vicinity of the critical point.

4. Unified fundamental equation of state for SF$_6$ 
In order to develop UFEoS for SF$_6$, we have chosen a function $F^{(id)}(T, \rho)$ in accordance with [19]:

$$F^{(id)}(T, \rho) = \ln \omega + a_1 + \frac{a_2}{T} - (f_1 - 1) \ln T - \sum_{i=2}^{6} \frac{f_i g_i}{T} + \sum_{i=2}^{6} f_i \ln \left[ \exp \left( \frac{g_i}{T} \right) - 1 \right],$$  

(12)

where $f_1 = 3.9837756784$; $f_2 = 2.2181851010$; $f_3 = 10.921337374$; $f_4 = 3.3102497939$; $f_5 = 17.518967483$; $f_6 = 2.8903523803$; $g_2 = 1114.38$; $g_3 = 925.64$; $g_4 = 499.26$; $g_5 = 884.90$; $g_6 = 1363.93$; $a_1 = 1.8009691417$; $a_2 = 3447.899076$.

Coefficients and parameters of the fundamental equation of state (10) were calculated on the basis of an array of experimental data [26,31–39]. As a result, the following values of coefficients $D_i$ and parameters of UFEoS (10) were obtained: $T_c = 318.72509$ K; $p_c = 3.754981$ MPa; $\rho_c = 742.3$ kg/m$^3$; $R = 56.927$ J/(K × kg); $\alpha = 0.11$ and $\gamma = 1.24$; $\beta = (2 - \alpha - \gamma)/2$; $\delta = 1 + \gamma/\beta$; $D_1 = 0.69714199719673$; $D_2 = 1.0093824655266$; $D_3 = 5.028097301503601 \times 10^{-3}$; $u_0 = 4.54936419383512$; $x_0 = 0.456$. The values of coefficients $C_{i,j}$ are shown in tables 1 and 2.

Fundamental equation of state (10) transmits experimental $p$, $\rho$, $T$ data [26] within the experimental error (figure 1). When describing isobaric heat capacity, we have corrected the data of [27] for pressure by 0.17 MPa (in [6, 20], these data were adjusted for 0.18 MPa and experimental error (figure 1). When describing isobaric heat capacity, we have corrected the position of isobaric heat capacity maxima using a power function of the form. Note that in this case, we were taking into account both maxima of $C_p$ and parameters of UFEoS (10) were obtained:

- in the case of $T_c = 318.72509$ K; $p_c = 3.754981$ MPa; $\rho_c = 742.3$ kg/m$^3$; $R = 56.927$ J/(K × kg); $\alpha = 0.11$ and $\gamma = 1.24$; $\beta = (2 - \alpha - \gamma)/2$; $\delta = 1 + \gamma/\beta$; $D_1 = 0.69714199719673$; $D_2 = 1.0093824655266$; $D_3 = 5.028097301503601 \times 10^{-3}$; $u_0 = 4.54936419383512$; $x_0 = 0.456$. The values of coefficients $C_{i,j}$ are shown in tables 1 and 2.

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![Figure 1. Relative density deviations of SF$_6$ in the single-phase region calculated by UFEoS (10) from the data [26] on isotherms: 1 – 319.438 K; 2 – 321.137 K; 3 – 324 K; 4 – 328.135 K; 5 – 333.134 K; 6 – 340 K.](image-url)
Table 1. Coefficients $C_{i,j}$ of UFEoS (10).

| $i$ | 0   | 1     | 2     |
|-----|-----|-------|-------|
| 0   | 0   | 0     | 1.4637770371566 |
| 1   | 0   | 0     | −0.63299726030463 |
| 2   | 0   | 0     | −6.9345245487806 |
| 3   | 0   | −1.6847143908384 | 4.6626126469233 |
| 4   | 0   | 2.4857301151688 | 17.780809023334 |
| 5   | 0   | −2.2094331625811 | −22.791584602246 |
| 6   | −0.59534854821080 | −7.7913904062672 | −23.053391487337 |
| 7   | 0.42017808971155 | 8.0240007114335 | 48.314852275737 |
| 8   | 0.8887214598099 | 8.2537264492195 | 7.374530987776 |
| 9   | −0.25369277256102 | −6.1979865517789 | −48.204195267504 |
| 10  | −1.1564054457741 | −10.950107253019 | 9.859140112117 |
| 11  | −0.23910245749403 | 2.997623644224 | 24.656400405882 |
| 12  | 2.3889402148356 | 16.1635162129440 | −10.838347731068 |
| 13  | −0.93470071694943 | −6.1025917258811 | −5.445658177924 |
| 14  | −2.43943040099198 | −13.836052878828 | 3.889841136412 |
| 15  | 2.3097494234175 | 9.6198428241683 | 0 |
| 16  | 0.64151858416218 | 4.28099096318 | −0.3212556658286 |
| 17  | −1.7927712509113 | −5.953605883911 | 0 |
| 18  | 0.64173470052588 | 0.91028579975106 | 0.017503025420557 |
| 19  | 0.3303829387355 | 1.087099884378 | 0 |
| 20  | −0.34535514388404 | −0.5526410242851 | 0 |
| 21  | 0.10874182286637 | 0.085269378759387 | 0 |
| 22  | −0.012450084875819 | −0.001721828924938 | −8.7427358258199 $\times 10^{-5}$ |

Figure 2. Behavior of isobaric heat capacity of SF$_6$ in the critical region: 1, 4, 7, 10, 13, 16 – experimental data [27]. Isobars: (3.8, 3.85, 3.9, 3.95 and 4.0) MPa: 2, 5, 8, 11, 14 – calculation by UFEoS (10) (the pressure is corrected by +0.17 MPa); 3, 6, 9, 12, 15 – calculation by FEoS [20]; 16 – maximum values of $C_p$ on isobars 3.8 MPa, 3.9 MPa and 4 MPa [6]. Taking into account the possible shift of $p$ in the measurements of $C_p$ [27], the authors of [6] and [19] corrected the pressure by +0.18 MPa and +0.15 MPa respectively.
Table 2. Coefficients $C_{i,j}$ of UFeoS (10).

|   | 3     | 4     | 5    | 6    |
|---|-------|-------|------|------|
| 0 | -5.513975846793 | -5.8404813832234 | -10.945999836483 | 0.025913929421254 |
| 1 | 9.1949117966815 | 14.20085984305 | 18.4119389741 | 0.08325965097618 |
| 2 | -3.9464341029674 | -10.606203065316 | 0 | 0 |
| 3 | -1.2171568713294 | 6.1550036480068 | 0 | 0 |
| 4 | 33.420263912343 | 28.685681356182 | 0 | 0 |
| 5 | -58.801187014852 | -81.204281715646 | -36.44240476234 | 0 |
| 6 | -19.981253671732 | 19.220925805166 | 31.730353485532 | 0 |
| 7 | 96.144462211396 | 84.488094616614 | 12.450671904708 | 0 |
| 8 | -26.239298489294 | -55.417251177427 | -20.621114170845 | 0 |
| 9 | -54.847869551594 | -18.907648710798 | 5.5593475136811 | 0 |
| 10 | 29.684232657295 | 24.34781443569 | 0 | 0 |
| 11 | 9.6449901733389 | -4.9603340543263 | 0 | 0 |
| 12 | -8.0208947207762 | -0.23298976230222 | 0 | 0 |
| 13 | 0 | 0 | 0 | 0 |
| 14 | 0.48509984914474 | 0 | 0 | 0 |

Figure 3. Velocity of sound of SF$_6$ in a single-phase region on the critical isochore: 1, 2, 3 – experimental data [28]; 4 – calculation by UFeoS (10); 5 – calculation by FEnS [20]; 6 – calculation by FEnS [6].

5. Summary

On the basis of the new representation of a large-scale hypothesis in the form of (3), UFeoS (10) for sulfur hexafluoride has been developed. While calculating the equilibrium properties in the regular part of the thermodynamic surface, this UFeoS is not inferior to FEnS [19, 20] and with less uncertainty describes the wide vicinity of the critical point compared to the FEnS [6].

It is shown that unlike FEnS [6,20], UFeoS (10) qualitatively correctly transmits the behavior of the maxima line of isobaric heat capacity and the velocity of sound in the vicinity of the critical point (figure 2 and 3).
6. Conclusion

Based on the performed analysis, we can recommend UFEoS (10) for calculating equilibrium properties of sulphur hexafluoride in all the area of state parameters without restriction including the vicinity of the critical point and metastable states.

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