A model system of the liquid density, the gas density and the pressure on the saturation line of SF$_6$

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Abstract. We have set a task to develop a system of self-consistent models in the article. The first and the second models let us describe the liquid density and the gas density on the saturation line; the third one is connected with the saturation pressure. To build these models, we have used a methodical approach based on the Clapeyron–Clausius equation. The approach also includes some requirements of the scaling theory of critical phenomena. To calculate the adjustable coefficients of these models, experimental data on the liquid density, the gas density and the saturated pressure of SF$_6$ have been selected. The new system let us describe the named properties in a wide interval of temperature. A comparative study has been made for these calculated properties as well as for the mean diameter of the coexistence curve. Numerical results of the study are discussed.

1. Introduction

Our analysis of [1–16] has shown the following position.

- It is an urgent problem to modernize some models described properties on the saturation line:
  - $\rho^+(T)$ is used for the liquid density;
  - $\rho^-(T)$ is used for the gas density;
  - $p_s(T)$ is used for the saturation pressure.

  These models have to follow to the modern scaling theory of critical phenomena (ST).

- It is an interesting practical problem to develop a system of self-consistent equations; this system will includes:
  - equations $\rho = \rho^-(T)$ and $\rho = \rho^+(T)$, which describe the densities ($\rho^+$, $\rho^-$) in the range from $T_L$ to $T_c$, here $T_c$ is the critical temperature;
  - the equation $p = p_s(T)$, which describes the saturated steam pressure in the range from $T_L$ to $T_c$;
  - the equation $dp/dT = p'_s(T)$, which describes the derivative $p'_s(T)$ in the range from $T_L$ to $T_c$;
  - the equation $r^* = r^*(T)$, which describes a seeming heat $r^*$, which is linked with the heat of vaporization $r$ by the equation:

$$r^*(T) = r(T)/(1 - \rho^-/\rho^+).$$

(1)
We underline: $r^*$ is the value, which is experimentally determined.

The practical problem is connected with the error limits of the system. We pay attention to the equation of state (EOS) [17–19]. This EOS includes: a regular part, which is valid in the regular region of the thermodynamic surface, a scaling part, which is valid in the critical region and in the region of metastable states. Our estimates have shown that it is possible to improve the accuracy of such kind of EOS’s if we prepare special input arrays, which consist of experimental and calculated properties. We plan to build such arrays, which include heterogeneous reliable properties: ($\rho^-$, $T$) data, ($\rho^+$, $T$) data and ($p_s$, $T$) data in the range from the triple point ($p_t$, $T$, $\rho_t$) to the critical point ($p_c$, $T_c$, $\rho_c$).

The theoretical problem is connected with some requirements related to the scaling theory (ST) of critical phenomena [20]. The desired system has to meet these requirements. Some theoretical justification of models ($\rho^+ (T)$, $\rho^-(T)$, $p_s(T)$) is given in [1–7]. There are numerical data, which are placed in [9–13] and related to models ($\rho^+ (T)$, $\rho^-(T)$, $p_s(T)$). This group has to describe ($\rho^+$, $\rho^-$, $p_s$, $T$) data only in the critical region. The group includes: a Wegner’s model [13] and [2$\beta$] model [1,7,8].

Another group is developed in [14–16] and can describe ($\rho^+$, $\rho^-$, $p_s$, $p_s'$, $r^*$, $T$) data in the range from $T_t$ to $T_c$.

In this work, we have set the following goals:

- to develop the desired system (A), which has included self-consistent equations ($\rho^-(T)$, $\rho^+(T)$, $p_s(T)$) and satisfied the Wegner’s model;
- to develop the desired system (B), which has included self-consistent equations ($\rho^-(T)$, $\rho^+(T)$, $p_s(T)$), satisfied [2$\beta$] model and used the Clapeyron–Clausius equation as well as the function $r^*(T)$ [14];
- to compare numerical characteristics of the systems (A) and (B); these systems will be based on the same array of accurate experimental ($\rho^+$, $\rho^-$, $p_s$, $T$) data of sulfur hexafluoride presented in [21] in the temperature range from $T_t$ to $T_c$;
- to check structure variants included exponents ($\beta$, $2\beta$, $\beta + \Delta$, $1 - \alpha$, $3\beta$) and argument, $\tau = T/T_c - 1$.

### 2. Development of the [2$\beta$] model and the Wegner’s model based on the Clapeyron–Clausius equation

There is an equation $\rho^-(T)$ [15], which has been developed on the basis of the Clapeyron–Clausius equation:

$$\frac{dp_s}{dT} = \frac{r \rho^+ \rho^-}{T (\rho^+ - \rho^-)} = \frac{r^* \rho^-}{T},$$

where $r$ is the heat of vaporization which is associated with the “apparent” heat of vaporization $r^*$ by the dependence $r^*(T) = r(T)/(1 - \rho^-/\rho^+)$.

Directly from equation (2), the expression for the density $\rho^-(T)$ follows as a function:

$$\rho^-(T) = T p_s'(T)/r^*(T).$$

We have chosen the function $r^*(T)$ in the following form [11,15]:

$$r^*(T) = \frac{p_c}{p_c} \left( d_0 + d_1 |\tau|^\beta + d_2 |\tau|^2\beta + d_3 |\tau|^3\beta + \Delta + d_4 |\tau| \sum_{i=5}^{8} d_i |\tau|^{m(i)} \right),$$

where $d_i$ are constant coefficients; $\alpha$, $\beta$ and $\Delta$ are critical indices.
We have chosen the model \( p_s(T) \) in the form of the equation proposed in [16]:

\[
p_s(T) = p_c \exp \left( -\frac{a_0 \tau^2}{t} \right) \left( 1 + a_1 \tau + a_2 \tau^{2-\alpha} + a_3 \tau^{2-\alpha+\Delta} + \sum_{i=4}^{6} a_i \tau^{n(i)} \right),
\]

(5)

where \( a_i \) are constant coefficients; \( t = T/T_c \); \( n(i) \in N \).

The model \( \rho^-(T) \) is obtained by substituting expressions (4), (5) into equation (3):

\[
\rho^- = T \rho_c \frac{d}{dT} \left( \exp \left( -\frac{a_0 \tau^2}{t} \right) \left( 1 + a_1 \tau + a_2 \tau^{2-\alpha} + a_3 \tau^{2-\alpha+\Delta} + \sum_{i=4}^{6} a_i \tau^{n(i)} \right) \right) \times \left( d_0 + d_1 |\tau|^{\beta} + d_2 |\tau|^{2\beta} + d_3 |\tau|^{\beta+\Delta} + d_4 |\tau|^{1-\alpha} + \sum_{i=5}^{8} d_i |\tau|^{m(i)} \right)^{-1},
\]

(6)

where \( d_2 = d_2^2/d_0; \ m(i) = 1 + (i - 5)\beta \).

We require the implementation of the equality \( a_1 = d_0 \) [15]. In this case, from expression (6), when \( \tau \to 0 \), we get the model \( \rho^-(T) \), which works in the critical region:

\[
\rho^- = \rho_c \left[ 1 - D_1 |\tau|^{\beta} - D_2 |\tau|^{\beta+\Delta} + D_3 |\tau|^{2\beta} \right.
\]

\[
+D_4 |\tau|^{1-\alpha} + D_5 |\tau|^{3\beta} + D_6 |\tau|^{4} + o(|\tau|) \right],
\]

(7)

where:

\[
D_1 = \frac{d_1}{d_0}, \quad D_2 = \frac{d_3}{d_0},
\]

(8)

\[
D_3 = \left( \frac{d_2^2}{d_0} - \frac{d_2}{d_0} \right), \quad D_4 = \frac{d_4}{d_0} + \left( \frac{a_2}{d_0} \right) (2 - \alpha),
\]

(9)

\[
D_5 = - \left[ \left( \frac{d_4}{d_0} \right)^3 - 2 \frac{d_1 d_2}{d_0 d_0} \right], \quad D_6 = \left( 1 + \frac{d_5}{d_0} - 2 \frac{a_0}{d_0} \right).
\]

(10)

The structure of the function \( \rho = \rho^+(T) \) in the vicinity of the critical point should be consistent with expression (1) [21]. Therefore, we choose a function \( \rho = \rho^+(T) \) in accordance with the recommendations of [12] in the form of the following dependency:

\[
\rho^+(T) = \rho_c \left( 1 + D_1 |\tau|^{\beta} + D_2 |\tau|^{\beta+\Delta} + D_3 |\tau|^{2\beta} \right.
\]

\[
+D_4 |\tau|^{1-\alpha} + D_5 |\tau|^{3\beta} + D_6 * |\tau| + \sum_{i=7}^{13} D_i |\tau|^{k(i)} \right),
\]

(11)

where \( k(i) = 1 + (i - 5)\alpha \). Equations (6), (11) correspond to the Wegner’s mean diameter model [13], \( d_f \sim |\tau|^{1-\alpha} \) if we admit the condition

\[
D_3 = -D_3, \quad D_4 = -D_4, \quad D_5 = D_5.
\]

(12)

If equality (12) are performed, then near the critical point, we will get the following expressions for the order parameter: \( d_x = (\rho^+ - \rho^-)/(2\rho_c) \) and mean diameter \( d_f = (\rho^+ + \rho^-)/(2\rho_c) - 1 \):

\[
d_x = D_1 |\tau|^{\beta} + D_2 |\tau|^{\beta+\Delta} + o \left( |\tau|^{\beta+\Delta} \right), \quad d_f = D_4 |\tau|^{1-\alpha} + o \left( |\tau|^{1-\alpha} \right).
\]

(13)

Equations (6), (11) correspond to the mean diameter model [2\beta], \( d_f \sim |\tau|^{2\beta} \), if we admit the condition

\[
D_3 = D_3, \quad D_4 = D_4, \quad D_5 = D_5.
\]

(14)
Table 1. Parameters and coefficients of equations (5) [20].

| i  | a_i | i  | a_i | n(i) |
|----|-----|----|-----|------|
| 0  | 6.0 | 4  | 8.84873064 | 3    |
| 1  | 7.061104518 | 5  | 15.21516103 | 4    |
| 2  | 22.90993576  | 6  | 18.96462416 | 7    |
| 3  | -17.71425160 |    |      |      |

Table 2. Parameters and coefficients of equations (6).

| i  | d_i   | i  | d_i     | m(i) |
|----|-------|----|---------|------|
| 1  | 10.1136387176 | 5  | 2402.22723344 | 1    |
| 2  | 0.0343207842007 | 6  | -918.755594534 | 1.325|
| 3  | 1986.58448388  | 7  | 512.357326003  | 1.65 |
| 4  | -3825.62004986 | 8  | -141.072001428 | 1.975|

Table 3. Parameters and coefficients of equation (11), variant (12).

| i  | D_i   | k(i) | i  | D_i   | k(i) |
|----|-------|------|----|-------|------|
| 7  | -67174.4271858 | 1.11 | 11 | -1488474.19715 | 1.55 |
| 8  | 395022.671588  | 1.22 | 12 | 726296.490088  | 1.66 |
| 9  | -1078894.82144 | 1.33 | 13 | -149764.132660 | 1.77 |
| 10 | 1661824.66509  | 1.44 |  |      |      |

If equality (14) are performed, then near the critical point, we will get the following expressions for the order parameter and mean diameter $d_f$:

$$d_s = D_1|\tau|^{\beta} + D_2|\tau|^{\beta+\Delta} + o\left(|\tau|^{\beta+\Delta}\right), \quad d_f = D_3|\tau|^{2\beta} + o\left(|\tau|^{2\beta}\right).$$

Equations (6), (11) correspond to the mean diameter model $|2\beta|$ and $1-\alpha$, $d_f \sim |\tau|^{2\beta} + c|\tau|^{1-\alpha}$, if we admit the condition

$$D_3^* = D_3, \quad D_4^* = -D_4, \quad D_5^* = D_5.$$  (16)

If equality (16) are performed, then near the critical point, we will get the following expressions for mean diameter $d_f$:

$$d_f = D_3|\tau|^{2\beta} + D_4|\tau|^{1-\alpha} + o\left(|\tau|^{1-\alpha}\right).$$

Thus, using the same system of self-consistent equations (5), (6) and (11), we have got the opportunity to investigate both the Wegner’s, and the $|2\beta|$ mean diameter models.

Note that if in (11) the coefficients $|D_4^*|$ and $D_5^*$ satisfy the conditions $|D_4^*| \neq D_4$ and $|D_5^*| \neq D_5$, then for the function $\rho^-(T)$, we will obtain the model studied in [21].
### Table 4. Parameters and coefficients of equation (11), variant (14).

| i  | $D_i$       | $k(i)$ | i  | $D_i$       | $k(i)$ |
|----|-------------|--------|----|-------------|--------|
| 7  | −5487.03879333 | 1.11  | 11 | −166977.010355 | 1.55     |
| 8  | 37828.5540788  | 1.22  | 12 | 83073.4379689  | 1.66     |
| 9  | −112332.688616 | 1.33  | 13 | −17376.0963710 | 1.77     |
| 10 | 181186.009873  | 1.44  |    |              |         |

### Table 5. Parameters and coefficients of equation (11), variant (16).

| i  | $D_i$       | $k(i)$ | i  | $D_i$       | $k(i)$ |
|----|-------------|--------|----|-------------|--------|
| 7  | −72871.2148686 | 1.11  | 11 | −1684452.65233 | 1.55     |
| 8  | 435969.179680  | 1.22  | 12 | 825964.805167  | 1.66     |
| 9  | −1203441.96116 | 1.33  | 13 | −170989.737884 | 1.77     |
| 10 | 1868923.43577  | 1.44  |    |              |         |

**Figure 1.** Deviations $\delta p = (p_s^{(e)} - p_s^{(r)})/p_s^{(e)}$ 100% of the values $p_s^{(r)}$ calculated by equation (5) from the experimental [22] and tabular [23] values $p_s^{(e)}$: 1 – [22]; 2 – [23].

3. **Results**

Now we can proceed to the numerical analysis of equations (5), (6) and (11) under the following conditions:

- models $\rho^-(T)$, $\rho^+(T)$, $p_s(T)$ meet the requirements of ST;
- the parameters of these models should be calculated on the basis of statistical processing the experimental data [22].

In our approach, we have chosen the minimization criterion $U$ which includes some root-mean-square deviations (RMS) $S$: RMS of liquid density ($S_L$); RMS of gas density ($S_G$); RMS of saturated vapor pressure ($S_p$).

The following conditions were used:

- critical indices should be the same for all the models;
Figure 2. Deviations $\delta \rho^- = (\rho^- - \rho^-)^e (\rho^- - \rho^-)^r / \rho^e - \rho^r) 100\%$ of the values $\rho^r$ calculated by equation (6) from the experimental [22] and tabular [23] values $\rho^e$: 1 – [22]; 2 – [23].

Figure 3. Deviations $\delta \rho^+ = (\rho^+ - \rho^+_r)^e (\rho^+_r - \rho^+_r)^r / \rho^e + \rho^r) 100\%$ of the values $\rho^r$ calculated by equation (11) (variant (14)) from the experimental [22] and tabular [23] values $\rho^e$: 1 – [22]; 2 – [23].

Figure 4. Deviations $\delta \rho^+$ of the values $\rho^+_r$ calculated by equation (11) from the experimental values $\rho^+_e$ [22]: 1 – variant (14), (15); 2 – variant (12), (13); 3 – variant (16), (17).

- selection of critical indices ($\alpha = 0.11$, $\beta = 0.325$, $\Delta = 0.51$) has been realized on the basis of ST;
- critical parameters of sulfur hexafluoride: $p_c = 3.754$ MPa, $\rho_c = 742.26$ kg/m$^3$, $T_c = 318.71$ K.

As a result, we have two variants: the Wegner’s model (13) and the [2β] model (14) which are related to the parameters and coefficients of equations (5), (6) and (11). We will accept the coefficients of equations (5), (6) to be common for all considered variants of the phase equilibrium.
line. The values of these coefficients are presented in tables 1, 2. The coefficients of equation (11) are presented in tables 3–5.

Our comparison has shown that the system of self-consistent equations (5), (6) and (11) transmits experimental data \( (\rho^+, \rho^-, p_s, T) \) [22] in the case of the model \([2\beta]\) (14), (15) within the experimental error (figures 1–4) with less uncertainty than in the case of the Wegner’s model (13). Indeed, in case of (14), (15), RMS \( S \) of the calculated data from the experimental data [22] take the following values: \( S_p = 0.0022\% \), \( S_G = 0.0099\% \), \( S_L = 0.0016\% \).

In case of (12), (13) and (16), (17), the values of root-mean-square deviations \( S_p \) and \( S_G \) are the same as in case of (14), (15): \( S_p = 0.0022\% \), \( S_G = 0.0099\% \). At the same time, the uncertainty in calculating the density of a saturated liquid \( \rho^+ \) according to the Wegner’s model \( (S_L = 0.012\%) \) and the model \( d_f(17) \) \( (S_L = 0.0146\%) \) is significantly higher than in case of the \([2\beta]\) model \( (S_L = 0.0016\%) \).

4. Discussion
A system of self-consistent \( \rho^-(T), \rho^+(T), p_s(T) \) models has been developed. We have considered three variants of the systems of equations (5), (6) and (11): variant (12), (13) and (16), (17) has been developed on the basis of the \([2\beta]\) model [1, 8]; variant (14), (15) can be associated with the Wegner’s model [13]. The proposed approach has been tested on the example of describing the phase equilibrium line of sulfur hexafluoride. Our analysis of the results obtained confirms that according to the \([2\beta]\) model (5), (6), (11), (14), the deviations of the experimental data [22] do not exceed the experimental error of data [22] in the temperature range from the triple point to the critical point. These deviations can be characterized by the following RMS values: \( S_p = 0.0022\% \), \( S_G = 0.0099\% \), \( S_L = 0.0016\% \).

5. Conclusion
Our analysis has shown that the mean diameter model \([2\beta]\) describes the experimental data on the phase equilibrium line of sulfur hexafluoride with a smaller error than the Wegner’s model does [13]. The results obtained can be used to develop the EOS of sulfur hexafluoride based on the fundamental EOS [17–19], satisfying the requirements of the scaling hypothesis [20].

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