Method for constructing fundamental equation of state that satisfies the scaling theory and applicable for substances insufficiently explored in the critical point vicinity

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Abstract. Here, the authors discuss the problem of describing the equilibrium properties of a substance in the vicinity of the critical point on the basis of the fundamental equation of state (FEoS) of a liquid and a gas in the absence of experimental information about the calorific properties of a given substance in this field of state parameters. FEoS has the following characteristics: in the region of low densities, FEoS transforms to the virial equation of state; in the asymptotic vicinity of the critical point, FEoS meets the requirements of the scaling theory of critical phenomena. The method is based on a new representation of the scaling hypothesis based on the Scofield–Litster–Ho linear model (LM), the Benedek hypothesis and the Lysenkov–Rykov ratio (LR) which establishes the relationship between LM parameters and the real liquid using the Pokrovsky transformations. Testing of the proposed method for constructing FEoS has been carried out using the example of describing the equilibrium properties of argon. It has been ascertained that the use of the LR ratio has allowed, firstly, reducing the number of individual FEoS parameters and, secondly, excluding the data about isochoric heat capacity $C_V$ related to the critical point wide vicinity from the calculation scheme.

1. Introduction
Many researchers pay attention to the problem of describing the equilibrium properties of pure substances in a wide range of state parameters including the vicinity of the critical point. When describing the behavior of a substance in the asymptotic vicinity of the critical point, various approaches are used:

- scaling equations [1–4] and crossover equations of state [5–7] in parametric form [1, 2, 5, 6]
  and in variables of density ($\rho$) and temperature ($T$) [3, 4, 7];
- fundamental equations of state (FEoS) of the virial form [8–13];
- FEoS [14–23] taking into account the requirements of the scaling theory (ST) of the critical point [24].

We have analyzed the approaches [1–23] and came to the following results.
Scaling equations [1–4] and crossover equations [5–7] satisfy the requirements of ST [24], but have limited field of application in terms of state parameters.
FEoS [8–13] do not meet the requirements of ST [24]. Therefore, for example, in the vicinity of the critical point, FEoS [8–13] reproduce the sound speed $w$ and isochoric heat capacity $C_V$ with great uncertainty which increases unlimitedly when approaching the critical point. With that, for example, FEoS [8,9,12] describe the equilibrium properties of argon in the regular part of the thermodynamic surface with low uncertainty.

On the basis of the equation of state [13], the authors of [14] developed FEoS which took into account the peculiarity presence of isochoric heat capacity at the critical point. With that, FEoS [14] incorrectly reproduces the behavior of a number of thermodynamic functions in the vicinity of the critical point. For example, within the bounds of the approach [14], on the critical isochore, the behavior of the isothermal compressibility coefficient $K_T$ is described by the dependence $K_T \sim |\tau|^{-1}$, but it should be $K_T \sim |\tau|^{-\gamma}$ [24], $\tau = T/T_c - 1$, $\gamma \simeq 1.24$. The authors [3] found that the scaling function of the chemical potential $h(x)$ used in [14] can be calculated on the basis of the Migdal phenomenological theory of critical point [25] and the Benedek hypothesis [26]. However, meanwhile, the critical indices being part of FEoS [14] have to meet the following conditions: $\gamma = 3\beta$, $\delta = 4$ or $\gamma = 4\beta$, $\delta = 5$.

The authors of [15–21] submitted FEoS which describe the features of the thermodynamic surface in the vicinity of the critical point in accordance with ST [24]. On the basis of the phenomenological theory of the critical point [27], the authors of [20,21] developed FEoS for freon R218 and argon. These FEoS are not inferior to the scaling and crossover equations of state when describing thermodynamic surface in a wide vicinity of the critical point. With less uncertainty than FEoS [11], FEoS of R218 [20] transmits, firstly, experimental $p$, $\rho$, $T$ data in the dense liquid region and in the vicinity of the critical point, secondly, experimental data about $C_V$ in the vicinity of the critical point. When constructing FEoS, the authors of [15–21] used isochoric heat capacity data related to the vicinity of the critical point. With that, at present, for many working substances, experimental data about $C_V$ in the vicinity of the critical point are absent. This circumstance limits the use of methods for constructing FEoS [15–21].

2. Choosing the structure of FEoS

In this paper, basing on the approach [27], we have set a task to develop a method for constructing FEoS which:

(i) satisfies the requirements of the scaling theory [24] and is not inferior to the equations of state [2,7] when describing the vicinity of the critical point;
(ii) is not inferior to the equations of state [8,9,12] when describing the regular part of the thermodynamic surface;
(iii) contains only one individual parameter $x_0$ in the irregular component of the Helmholtz free energy. The value of this parameter is calculated on the basis of density data on the saturation line.

Implementation of paragraph iii allows using the approach proposed when developing FEoS of substances for which information about calorific properties is absent or limited in the vicinity of the critical point.

For constructing FEoS, we have used the results of [15,16,27] in which the Helmholtz free energy is given in the following form:

$$F(\rho,T) = F_{\text{reg}}(\rho,T) + F_{\text{nreg}}(\rho,T),$$

where $F_{\text{reg}}(\rho,T)$ is a regular function; $F_{\text{nreg}}(\rho,T)$ is an irregular function:

$$F_{\text{nreg}}(\rho,T) = RT_cZ_c\phi(\omega,t)|\Delta\rho|^{\delta+1}a(x),$$

where $\Delta\rho = \rho - \rho_c$, $\phi(\omega,t)$ is the scaling function of the chemical potential $h(x)$, $Z_c$ is the compressibility factor, $\omega$ is the wave number, $t$ is the temperature, $\Delta\rho$ is the deviation of the density from the critical density, $a(x)$ is the function of the density $\rho$.
where \( \phi(\omega, t) \) is a crossover function; \( Z_c = p_c/(R\rho_cT_c) \times 10^{-2} \) is the critical compressibility; \( R \) is the gas constant; \( p_c \) is the critical pressure; \( \Delta \rho = \omega - 1; \omega = \rho/\rho_c; x = \tau/|\Delta \rho|^{1/3} \) is the scaling variable; \( t = T/T_c \).

The scaling function \( a(x) \) is calculated on the basis of a new representation of the scaling hypothesis [27] and the Benedek hypothesis [26]. The function \( a(x) \) has the following structure [20]:

\[
a(x) = -\frac{u_0 Z_c k \gamma}{2 a b^2 \alpha_1 (1 - \varepsilon)} [(\varphi + \varphi_1)^{2-\alpha} - \varepsilon (\varphi + \varphi_2)^{2-\alpha}] + \frac{u_0 Z_c x^\gamma}{2 k} (\varphi + \varphi_3)^\gamma + C, \tag{3}
\]

where \( \varepsilon = x_1/x_2; \alpha_1 = (2 - \alpha)(1 - \alpha); \gamma_1 = \gamma(\gamma - 1); u_0 \) is the individual parameter; \( \varphi = x/x_0; \varphi_1 = x_1/x_0, i \in \{1, 2, 3\}; x_0 \) is the value of the scaling variable \( x \) on the saturation line; \( b^2 = (\gamma - 2\beta)/[\gamma(1 - 2\beta)] \); \( k = [(b^2 - 1)/x_0]^\beta; C \) is the constant coefficient which value is found from the equation \( (\delta + 1)(\varphi = -1) + x_0/\beta a^2(\varphi = -1) = 0 \).

We have selected the regular component (1) in such a way that in the region of low densities, the function \( F_{reg}(\rho, T) \) would provide the transition of (1) to the virial equation and carrying out the requirement \( p(\rho_c, T_c) = p_c \). As a result, for the function \( F_{reg} \), we have got the following expression:

\[
F_{reg}(\rho, T) = F^0(\rho, T) + RT \omega y_2 + RT \omega (Z_c - 0.2) y_6 + RT \omega D_3 (y_4 - y_6) + RT \omega \tau_1 [D_1 (\omega - 3) + D_2 (\omega^2 - 2\omega)] + RT \omega \sum_{i=0}^{2} \sum_{j=0}^{8} \left[C_{i,j} \tau_i^\gamma \Delta \rho^j\right], \tag{4}
\]

where \( F^0(\rho, T) \) is the ideal gas component of \( F(\rho, T) \); \( \tau_1 = T_c/T - 1; \) functions \( y_2, y_4, y_6 \) have the following form: \( y_2 = -7.7/6 + 2.9/6 \Delta \rho - 1.1/6 \Delta \rho^2 + 0.05 \Delta \rho^3; y_4 = 5 - 4 \Delta \rho + 3 \Delta \rho^2 - 2 \Delta \rho^3 + \Delta \rho^4; y_6 = 4 - 3 \Delta \rho + 2 \Delta \rho^2 - \Delta \rho^3 + \Delta \rho^5 \).

We have calculated \( \varphi_1, \varphi_2, \varphi_3 \) according to the method [28] with \( \gamma = 1.24 \) and \( \delta = 4.815 \); \( \varphi_1 = 2.82243463943; \varphi_2 = 14.6824028781; \varphi_3 = 7.80705857699 \).

In [29], on the basis of the Pokrovsky transformations, there was established relationship between the parameters \( u_0 \) and \( k \) of the symmetric system described by LM and the corresponding parameters \( u_p \) and \( k_p \) of the real liquid (the Lysenkov–Rykov ratio):

\[
k u_0^{-1/\delta} = k_p u_p^{-1/\delta}. \tag{5}
\]

Here

\[
k_p = k(1 - uv)^\beta, \quad u_p = u_0(1 - uv)^{\beta}, \tag{6}
\]

where \( u \) and \( v \) are the Pokrovsky transformation parameters.

Note that often, when describing a real liquid, due to the small value of the parameter \( u \), one accepts \( u = 0 \) [14].

It was also shown in [29] that the dependence of the complex \( k_p u_p^{-1/\delta} \) on the critical compressibility \( Z_c = p_c/(R\rho_c T_c) \) is a linear function:

\[
k_p u_p^{-1/\delta} = A + B Z_c, \tag{7}
\]

where \( A \) and \( B \) are constants, the values of which depend on the choice of critical indices [29].

On the basis of expressions (5)–(7), meeting the condition \( u = 0 \), we have obtained the following dependence for the parameter \( u_0 \):

\[
u_0 = \left[ k(1 - uv)^\beta \right]^{-\delta/\beta} \left[ A + B Z_c \right]^{-\delta, \tag{8}\right]
\]

We have calculated the values of the constants \( A \) and \( B \) on the basis of information about the values \( k \) and \( u_0 \) given in [30–32]: \( A = 1.2687470329251 \) and \( B = -2.2988501100973 \). Formula (8)
Table 1. Coefficients $C_{i,j}$ of FEoS (1).

| $i$ | 0    | 1                  | 2                  |
|-----|------|--------------------|--------------------|
| 0   | 0    | 0.00              | 2.4148388469485    |
| 1   | 0    | 0.00              | -1.9726058717959   |
| 2   | 0    | 0.00              | 2.689041361259     |
| 3   | 0    | -1.528769121223   | 1.2224905628239    |
| 4   | 0    | 2.924947311287    | 3.526646751111     |
| 5   | 0    | -0.1731743253057  | 0.436674688772     |
| 6   | -0.27306772162636 | -0.70349320674424 | 0.19938263724407   |
| 7   | -0.05798720000981 | 3.5203397636453    | 3.9696637431805    |
| 8   | -0.10383696478211 | -4.8852250300494   | -4.15095195535     |
| 9   | 0.478770180236    | 1.957387707743     | 4.997803831529     |
| 10  | -0.82960388729933 | 4.9704295645022    | -1.165062412876    |
| 11  | -0.68687760584463 | -5.859080232005    | -3.052856346891    |
| 12  | 1.91125311404343  | -2.3417236151507   | 2.097930787939     |
| 13  | -1.0835345316331  | 5.9188892479841    | 0.2572055917058    |
| 14  | -0.82118068183532 | -1.2899805176031   | -0.8012302076035   |
| 15  | 1.3393055734044   | -3.0554901249901   | 0.0002821339375858 |
| 16  | -0.50220327351296 | 2.408480237001     | 0.3283719436998    |
| 17  | -0.21670933564854 | -0.18086551562867  | -0.1414204953293   |
| 18  | 0.3037348189265   | -0.62503784571879  | 0.0002806482773624 |
| 19  | -0.14260762551212 | 0.3909302749512    | 0.01338364285165   |
| 20  | 0.036000271709751 | -0.1120879028463   | -0.00280648277362  |
| 21  | -0.004890078228154 | 0.016470019380175  | 0.0002821339375858 |
| 22  | 0.0002821339375858 | -0.001005338882154 | 3.5269333638806 x 10^-5 |

is valid in the case of $\gamma \approx 1.24$ and $\delta \approx 4.8$. With the values $\gamma = 1.24$ and $\delta = 4.815$, from (8), for argon, we have obtained the following result: $u_0 = 14.419376715041$.

We have chosen the crossover function $\phi(\omega,t)$ in compliance with the recommendations [20]:

$$
\phi(\omega,t) = \phi_0(\omega) \phi_1(t), \quad \phi_0(\omega) = \left[ (1 - \omega)^3 - 1 \right]^2, \quad \phi_1(t) = 1/t^2. \quad (9)
$$

We have conducted testing the proposed method of constructing FEoS (1)–(4) using the example of describing the equilibrium properties of argon – a substance for which reliable experimental information exists in a wide range of state parameters [33–55].

3. Testing the method proposed using the example of constructing FEoS of argon

We have chosen the ideal gas component of argon $F^0(T,\rho)$ in compliance with the recommendations [7]:

$$
F^0(\rho,T) = RT \left( \ln \omega + a_{1}^0 \omega^{-1} + a_{2}^0 \omega^{-1} - 1.5 \ln t \right), \quad (10)
$$

where $a_{1}^0 = 58.31666243$ and $a_{2}^0 = 524.94651164$.

The coefficients of FEoS (1)–(4) have been determined on the basis of experimental information [33–49]. As a result, for the coefficients and parameters of equations (1)–(4), the following values have been obtained: $T_c = 150.66$ K; $p_c = 48.634$ MPa; $\rho_c =$
Table 2. Coefficients $C_{i,j}$ of FEoS (1).

|   | 3          | 4          | 5          |
|---|------------|------------|------------|
| 0 | 4.002772397655 | 1.738838171652 | 0.1826760184779 |
| 1 | −2.9492579440065 | −0.42046568940555 | 0.5611690921191 |
| 2 | −0.97611602134862 | −4.91476880197097 | −2.9250032573085 |
| 3 | 5.5919533963043 | 4.5503005330464 | 2.4636166684809 |
| 4 | 1.2851637953711 | 1.4244003188083 | 0.5518718378057 |
| 5 | −2.0237401975022 | −3.8352563208319 | −1.4570960452668 |
| 6 | 2.942820483947 | 2.76145453742994 | 0.6239948406494 |
| 7 | 0.6962473466708 | −1.3503072611532 | −0.089056016657128 |
| 8 | −1.7453780826824 | −0.090118475463677 | 0 |
| 9 | 2.3653760497926 | 0.84597263472887 | 0 |
| 10 | −1.0829266705652 | −0.63979636215182 | 0 |
| 11 | 0.1028361430572 | 0.23177308579523 | 0 |
| 12 | −0.047550042089277 | −0.044330189356126 | 0 |
| 13 | 0.0037413925160214 | 0.0037529135828289 | 0 |

535.1 kg/m³; $R = 0.2081332$ J/(g×K); $u_0 Z_c = 4.1699193124581$; $D_1 = 0.51350525218839$; $D_2 = 0.90286908345406$; $D_3 = −8.075978759347501 \times 10^{-3}$; $\alpha = 0.112$, $\gamma = 1.24$; $x_0 = 0.309543019423109$. The values of the coefficients $C_{i,j}$ are presented in tables 1 and 2.

The root-mean square deviation (RMS) [56] $S_\rho$ of the density values $\rho^{(e)}$ in the single-phase region calculated by FEoS (1)–(4) from the experimental data $\rho^{(e)}$ [34, 36–38, 43–45] made:

$S_\rho = 0.135\%$ [45], $S_\rho = 0.372\%$ [43], $S_\rho = 0.251\%$ [36], $S_\rho = 0.081\%$ [37], $S_\rho = 0.172\%$ [38], $S_\rho = 0.673\%$ [10], $S_\rho = 0.243\%$ [34].

In the vicinity of the critical point (figure 1) and in the high-temperature region (figure 2), the FEoS proposed (1)–(4) reproduces $p$, $\rho$, $T$ data within the experimental uncertainty of the data [35] and agrees well with the calculated data [2, 7, 9, 10]. In the near-critical region, RMS $S_p$ and $S_\rho$ of the pressures $p^{(e)}$ calculated by FEoS (1) for the experimental data $\rho^{(e)}$ and $p^{(e)}$ [35] have made: $S_p = 0.72\%$, pressure $S_\rho = 0.036\%$.

Note that when searching for the FEoS parameters, experimental information about
Figure 1. Relative deviations $\delta p$, $\delta p = (p^{(e)} - p^{(r)}) / p^{(e)}$100%; $p^{(r)}$, $\rho$, $T$ data calculated on the base of FEoS (1); experimental $p^{(e)}$, $\rho$, $T$ data from [34]; the isotherms: 1 – 148.007 K; 2 – 149.006 K; 3 – 149.598 K; 4 – 149.983 K; 5 – 150.372 K; 6 – 150.52 K; 7 – 150.579 K; 8 – 150.621 K.

Figure 2. Relative deviations $\delta \rho$, $\delta \rho = (\rho^{(e)} - \rho^{(r)}) / \rho^{(e)}$100%; $\rho^{(r)}$, $\rho$, $T$ data calculated on the base of FEoS (1); 1, 2 – $\rho^{(e)}$, $\rho$, $T$ data calculated on the base of FEoS [9]; 3 – $\rho^{(e)}$, $\rho$, $T$ data from [10]; the isotherms: 1, 3 – 2300 K, 2 – 17000 K.

Figure 3. Behavior of $C_V$ in a single-phase region: 1 – $C_V$, $\rho$, $T$ data calculated on the base of FEoS (1), the isochore ($\rho = 541.9$ kg/m$^3$); 2 – $C_V$, $\rho$, $T$ data calculated on the base of FEoS [9], the isochore ($\rho = 541.9$ kg/m$^3$); 3 – experimental $C_V$, $\rho$, $T$ data from [50], the isochore ($\rho = 541.9$ kg/m$^3$); 4 – experimental $C_V$, $\rho$, $T$ data from [52], the isochore ($\rho = 541.9$ kg/m$^3$).
Figure 4. Behavior of \( C_V \) in a single-phase region: 1, 2, 3 – \( C_V, \rho, T \) data calculated on the base of FEoS (1); the isochors: 1 – 533.4 kg/m\(^3\), 2 – 565.7 kg/m\(^3\), 3 – 652 kg/m\(^3\); 4, 5, 6 – experimental \( C_V, \rho, T \) data from [51]; the isochors: 4 – 534.4 kg/m\(^3\), 5 – 565.5 kg/m\(^3\), 6 – 647.7 kg/m\(^3\); 7, 8, 9 – experimental \( C_V, \rho, T \) data from [52]; the isochors: 7 – 533 kg/m\(^3\), 8 – 560 kg/m\(^3\), 9 – 666 kg/m\(^3\).

Figure 5. Behavior of \( C_V \) in a single-phase region: 1, 2, 3, 4, 5 – experimental \( C_V, \rho, T \) data from [51]; the isochors: 1 – 541.9 kg/m\(^3\), 2 – 565.5 kg/m\(^3\), 3 – 604.4 kg/m\(^3\), 4 – 632.2 kg/m\(^3\); 5 – 647.7 kg/m\(^3\); 6, 7, 8, 9, 10 – \( C_V, \rho, T \) data calculated on the base of FEoS (1); the isochors: 6 – 541.9 kg/m\(^3\), 7 – 565.5 kg/m\(^3\), 8 – 604.4 kg/m\(^3\), 9 – 632.2 kg/m\(^3\), 10 – 647.7 kg/m\(^3\).

\( C_V \) [50–54] was excluded from the reference database. However, FEoS describes these data within their experimental uncertainty (figures 3–5). In the single-phase region, RMS \( S_{C_V} \) of isochoric heat capacity calculated by FEoS (1) for the experimental data [50, 51] has made: \( S_{C_V} = 2.7\% \) [50], \( S_{C_V} = 3.2\% \) [51]. With less uncertainty than the fundamental equations of state [8,9,12], FEoS (1) describes not only experimental information about \( C_V \) [50–54], but also experimental data about the sound speed \( w \) [55] in the vicinity of the critical point (figure 6).

Calculated values of properties from the FEoS (1) to verify computer code: \( T = 400 \) K, \( \rho = 1000 \) kg/m\(^3\), \( p(\rho,T) = 169516.183 \) kPa, \( C_V(\rho,T) = 0.3783236 \) kJ/(kg×K).
Figure 6. Behavior of $w$ in a single-phase region: 1, 4, 7, 10 – experimental $w$, $p$, $T$ data from [55]; 2, 5, 8, 11 – $w$, $p$, $T$ data calculated on the base of FEoS (1); 3, 6, 9, 12 – $w$, $p$, $T$ data calculated on the base of FEoS [9]; the isotherms: 1, 2, 3 – 150.694 K, 4, 5, 6 – 150.724 K; 7, 8, 9 – 150.8 K; 10, 11, 12 – 150.818 K.

4. Summary
FEoS (1)–(4) has been developed. In the first place, this FEoS works satisfactorily in a wide range of pressures and temperatures including the vicinity of the critical point. FEoS (1)–(4) has: (i) properties of the virial series in the regular part of the thermodynamic surface; (ii) meets the requirements of ST [24]; (iii) to determine the parameters of the singular component of FEoS (1)–(4), one requires knowledge of only critical indices, critical compressibility and parameter $x_0$ which can be found on the database about the saturation line.

5. Conclusion
The method proposed for constructing FEoS satisfying the scaling hypothesis can be recommended for developing state equations of both substances well studied in thermodynamic terms, but for which reliable information about isochoric heat capacity at the critical point is missing (sulfur hexafluoride, for example, belongs to these substances), and the ones poorly studied in the vicinity of the critical point (these substances include, for example, R1234yf, R1234ez, R236ea).

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Thermodynamic properties, coefficients of dynamic viscosity and thermal conductivity at temperatures of 85...1300 K and pressures of 0.1...1000 MPa (Liquid and gaseous argon. Argon zhidkiy i gazoobraznyy. Termodinamicheskiye svoystva, koeffitsiyenty dinamicheskoy vyazkosti i teploprovodnosti pri temperaturakh 85...1300 K i davleniyakh 0,1...1000 MPa) (Moscow: Standartinform)