Methods for calculating equilibrium properties of pure substances, considering the critical point features

S V Rykov, I V Kudryavtseva, V A Rykov, A V Zaitsev
ITMO University, 49 Kronvergskiy, Saint-Petersburg 197101, Russia

Abstract. This paper deals with a fundamental equation of state for matter (FEoS). When constructing FEoS, the method of pseudocritical points (PCP) is used. The PCP method is based on the Benedek hypothesis and a new representation of the scale hypothesis of the critical point. We show the possibility to construct FEoS of argon based on the PCP method with the following characteristics: (i) FEoS is transformed into the virial equation of state in the region of small densities; (ii) FEoS is transformed into the Widom equation in the region of the critical point; (iii) FEoS has its working area with pressure \((0 \leq p / p_c \leq 740)\), density \((0 \leq \rho / \rho_c \leq 3.2)\) and temperature \((83.8058 \leq T \leq 2300 ~K)\). We compare FEoS with a number of known equations of argon state and discuss the results.

1. Introduction
The problem of constructing fundamental equations of state (FEoS) attracted the attention of many researchers [1–10]. We have analyzed the approaches [1–10] that will allow us to get good results.

Article [1] represents an equation of state for argon that allows for calculations at high temperature \(p, \rho, T\) (up to 2300 ~K). The equation obtained in [1] has low accuracy as calculating \(p, \rho, T\) data in the temperature range \(300 \leq T \leq 1300 ~K\) leads to large errors in the density, \(\delta \rho \geq 1\%\), and pressure, \(\delta p \geq 2\%\). The working area of FEoS [2] is based on the pressure \((0 \leq p / p_c \leq 1000 ~\text{MPa})\) and temperature \((83 \leq T \leq 700 ~\text{K})\). FEoS in [1, 2] do not satisfy the requirements of the scale theory of the critical point [11]. Therefore, the speed of sound and the isochoric heat capacity in the vicinity of the critical point are described [2] with a significant error (up to 50 and more %).

Article [3] represents a crossover equation of state written in the density-temperature variables. There is a transition of the crossover equation to the Widom equation [13] in an asymptotic vicinity of the critical point. Our analysis has shown that the crossover equation [3] represents:

- experimental information on the heat capacity \(C_v\) [14] in the critical region with deviations significantly exceeding the error of these data;
- experimental information on the speed of sound [15] with large deviations, for example, from an array of 200 points of reference [15], the crossover equation [3] describes only 5 points within the experimental error.

The authors [4] proposed to solve the problem of FEoS constructing with the use of a combined equation that includes the following components:

- equation of state, related to a gas phase;
- scaling equation developed on the basis of the scale function of the chemical potential:

\[
h(x) = A \left[ \left( x + x_q \right)^\gamma + C \right]
\] (1)
where $x = \tau / |\Delta \rho|^{\alpha \beta}$ is the scaling variable; $\Delta \rho = \rho / \rho_c - 1$; $\tau = T / T_c - 1$; $\rho_c$ and $T_c$ are the critical density and critical temperature; $A$, $C$ and $x_q$ are constants; $\gamma$ is the critical index; and $\beta$ is the critical index of the coexistence curve.

According to our analysis the equation of state [4] with the scale function (1) incorrectly when describing the neighbourhood of the critical point reproduces qualitatively:

- critical isotherm, $\Delta \rho \square (\Delta \rho)^3$ that should be $\Delta \rho \square |\Delta \rho|^{\alpha - 1}$, $\Delta \rho = p / p_c - 1$;
- coefficient of isothermal compressibility $K_T$, $K_T|_{\rho \rightarrow \rho_c} \square |\tau|^{- 1}$ that should be $K_T|_{\rho \rightarrow \rho_c} \square |\tau|^{- \omega}$.

Other disadvantages of FEoS [4] are mentioned in [16–18].

2. FEoS structure: irregular component of Helmholtz free energy

This paper develops a fundamental equation for argon state that is based on the method of pseudocritical points (PCP) [5–7] and meets the following conditions:

a) FEoS has a satisfactory accuracy in comparison with that of a virial equation of state in a regular part of the thermodynamic surface;

b) FEoS has no mathematical difficulties discussed earlier and connected with the calculations of properties ($p$, $F$, $s$, $i$, $w$, $C_v$, $C_p$);

c) FEoS follows the laws of the scaling theory (ST) in the critical region.

We offer FEoS in the form [6]:

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

(2)

where $F(\rho, T)$ is the Helmholtz free energy; $F_{\text{reg}}(\rho, T)$ is the regular function; and $F_{\text{irreg}}(\rho, T)$ is the irregular component.

Component $F_{\text{irreg}}(\rho, T)$ is written in the form [17]:

$$F_{\text{irreg}}(\rho, T) = RT \phi(\omega, t)|\Delta \rho|^{\alpha + 1} a(x),$$

(3)

where $\phi(\omega, t)$ is the regular function; $p_c$ is the critical pressure; and $\omega = p / p_c$; $\delta$ is the critical index of the critical isotherm.

The scale function $a(x)$ is calculated on the basis of a new representation of the scale hypothesis [19]:

$$\Delta S^{\alpha / T} = \varphi_0 + \varphi_m m^2, m = \Delta \rho X^{\beta / T},$$

(4)

where $\Delta S = (\rho T_c / p_c) [S(\rho, T) - S_0(\rho, T)]$ is the reduced entropy; $S_0(\rho, T)$ is the regular function; $p_c$ is the critical pressure; $\omega = p / p_c$; $X$ is the singular component of the thermodynamic function $X$; and $\chi$ is the critical index of the function $X$ (for instance, $X = C_v$ and $\chi = \alpha$).

As a result, the function is represented in the form [19, 20]:

$$a(x) = A_1 (\varphi + \varphi_1)^{2 - a} + A_2 (\varphi + \varphi_2)^{2 - a} + B_1 (\varphi + \varphi_2)^{2 - a} + C,$$

(5)

where $A_1 = -D_0 k \gamma \varphi x_0^{2 - a} 2 \alpha b^2 \alpha_x (1 - \varepsilon) \gamma$; $A_2 = -\varepsilon A_1$; $B_1 = D_0 x_0^2 (2 k)^{-1}$; $\varepsilon = x / x_0$; $\alpha = (2 - \alpha)(1 - \alpha)$; $\gamma = \gamma(\gamma - 1)$; $u_0$ is the individual parameter; $\varphi = x / x_0$; $x_0$ is the value of $x = \tau / |\Delta \rho|^{\alpha \beta}$ on the saturation line; $b^2 = (\gamma - 2 \beta) / [\gamma(1 - 2 \beta)]$; $k = [b^2 - 1 / (x_0 - \varphi)^{\beta}]$; and $C$ is the constant that can be calculated from equation $h(x = x_0) = (\delta + 1) a(\varphi = x_0) + x_0 / (\beta \varphi a(\varphi = 0) = 0$.

In [20] ($\varphi_0$) parameters (5) are determined only by the critical indices. We have chosen the critical indices ($\alpha = 0.11$, $\beta = 0.325$, $\gamma = 1.24$, $\delta = 4.815$) on the basis of ST. Thus, ($\varphi_0$) parameters can be
applied with an accuracy that correlates with the accuracy of the critical indices. In this case, \( \varphi_i \) values can be expressed in the form: \( \varphi_1 = 2.80724769, \varphi_2 = 14.4717304, \varphi_3 = 5.73246825 \).

3. F EOS structure

The structure of F EOS (2) includes a number of components. The regular component \( F_{ij} (\rho,T) \) and function \( \phi(\omega,t) \) have been established considering the results of [5–7, 17].

First, it is necessary to meet some conditions connected with derivatives [5–7], that have the following forms

\[
\left( \frac{\partial^np}{\partial \rho^n} \right)_{T=T_c, \rho=\rho_c} = 0, \quad \left( \frac{\partial p}{\partial \rho} \right)_{T=\rho=\rho_c} = o(\tau),
\]

where \( n \in \{1, 2, 3, 4\} \), \( o \) is the Landau symbol.

Second, equation (2) can be converted to the Widom equation [13] in a vicinity of the critical point:

\[
\Delta \mu = \rho_c / p_c \left[ \mu (\rho, T) - \mu_c (T) \right] = \Delta \rho \left[ \delta + h(x) \right],
\]

where \( \mu \) is the chemical potential; and \( \mu_c (T) \) is the regular function.

Third, F EOS (2) can be converted to \( Z(\rho, T) \) in the field of rarefied gas. This \( Z(\rho, T) \) is the thermal equation of state that is based on equation [20] and has the following form:

\[
Z(\rho, T) = 1 + \omega_B(T) + \omega^2 C(T) + \ldots,
\]

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

As shown in [17], conditions (6), (7) and (8) are satisfied by the function:

\[
F(\rho, T) = F^0(\rho, T) + RT \omega y_2 + RT \omega (Z - 0.2)y_6 + RT \omega \tau_1 \left[ D_1 (\omega - 3) + D_2 (\omega^2 - 2\omega) \right] + RT \omega \sum_{i=0}^{N} \sum_{j=0}^{M} C_{i,j} \tau_1^i \Delta \rho^j + RT \phi(\omega, t) \left[ \Delta \rho \right]^{\delta + 1} a(x),
\]

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

We have considered various versions of crossover functions, for example, used in [4, 7, 17, 18]. Function \( \phi \) shows the best results in describing the equilibrium properties of argon:

\[
\phi(\omega, t) = \phi_0 (\omega) \delta_0 (t), \quad \phi_0 (\omega) = \left[ (\Delta \omega)^2 - 1 \right]^2, \quad \delta_0 (t) = 1 / t^2.
\]

In particular, equation (9) with the crossover function (10) satisfies the following requirements:

- it passes into the virial equation [21] in the region from a real gas with a low density;
- it passes into the Widom equation (7) in the vicinity of the critical point.

4. F EOS of argon

F EOS (9) with the crossover function (10) is tested by the case of argon properties. Argon has been chosen since it belongs to a group of substances well investigated in experiments with a regular part of the thermodynamic surface and in the vicinity of the critical point [12, 14, 23–28].

Function \( F^0 (T, \rho) \) in (9) is the ideal gas component of argon free energy [2]:

\[
F^0 (T, \rho) = RT \left( \ln \omega + a_0^0 + a_0^0 t^{-1} - 1.5 \ln t \right),
\]

3
where \(a_0^i=58.31666243\) and \(a_0^i = 524.94651164\).

The coefficients and parameters of FEoS (9) have been calculated on the basis of the array of experimental data [12, 14, 23–28]. As a consequence, the following values have been obtained for coefficients \((D_j)\) and other parameters \((9)\): \(T_1 = 150.66 \text{ K} \), \(p_r = 48,634 \text{ MPa} \), \(\rho_r = 535.1 \text{ kg/m}^3 \); \(R = 208.1332\) \text{ J/(K \cdot mol)}\); \(D_0 = 4.54936419383512\); \(D_1 = 0.49615873279042\); \(D_2 = 0.94224177278619\); \(D_3 = -7.8725653091375 \times 10^{-3} \); \(x_0 = 0.3106619960157\).

The values of coefficients \(C_{i,j}\) are presented in tables 1, 2 and 3.

### Table 1. The coefficients of FEoS (9).

| \(i\) | \(j\) | 0 | 1 | 2 |
|---|---|---|---|---|
| 0 | 0 | 0 | 2.7150069301782 |
| 1 | 0 | 0 | -2.475363392226 |
| 2 | 0 | 0 | -4.0921572499302 |
| 3 | 0 | -1.2784013959509 | 4.142219831138 |
| 4 | 0 | 0.86272883534777 | 6.759348441078 |
| 5 | 0 | -1.126301485585 | -10.76762429115 |
| 6 | -0.27209952299476 | -3.2250687951095 | -6.2590084795691 |
| 7 | -0.04248728866173 | 4.1185051071055 | 15.023962312325 |
| 8 | 0.65255052869088 | 1.852397676294 | -0.2095900917183 |
| 9 | 0.29214523747814 | -1.8851973312562 | -5.7611390827258 |
| 10 | -1.4551552224281 | -2.4685980943678 | 2.932235246132 |
| 11 | 0.23067871394673 | 1.303107117647 | 0.05669763939522 |
| 12 | 1.8809983056351 | 3.5664261992108 | -0.40913328364178 |
| 13 | -1.7166174504492 | -3.8982438304705 | 0.07759141658365 |
| 14 | -0.38185065443943 | -0.56735217113174 | 0 |
| 15 | 1.4551076338408 | 3.134439830403 | 0 |
| 16 | -0.77675330366795 | -1.776403724453 | 0.0023852503295424 |
| 17 | -0.11105260958357 | -0.19047759503284 | 0 |
| 18 | 0.32613422925281 | 0.70803438892297 | -0.0063214441786344 |
| 19 | -0.17543586891566 | -0.3912297925574 | 0 |
| 20 | 0.04796673948846 | 0.10870072197066 | 6.4293384745538 \times 10^{-3} |
| 21 | -0.0069187129521167 | -0.015882445881479 | 0 |
| 22 | 0.00041966292149754 | 0.00097435573490805 | -2.4949592372155 \times 10^{-6} |

### Table 2. The coefficients of FEoS (9).

| \(i\) | \(j\) | 3 | 4 | 5 |
|---|---|---|---|---|
| 0 | 4.1847960774079 | 1.0834912448788 | -0.017817824245948 |
| 1 | -3.7846379742591 | -0.94319175940691 | 0 |
| 2 | -9.6738083043926 | -4.800716700836 | 0 |
| 3 | 10.971860263865 | 5.8102903920162 | 0 |
| 4 | 11.699839345202 | 6.1086300184687 | 0 |
| 5 | -20.65888297077 | -11.61584427081 | 0 |
| 6 | -2.9879944058547 | 0 | 0 |
| 7 | 18.8622620692736 | 8.8145385193527 | 0 |
| 8 | -7.6230734248061 | -4.470679714421 | 0 |
| 9 | -3.8994015818 | -1.4185174033559 | 0 |
| 10 | 4.171451537935 | 2.0052774619115 | 0 |
| 11 | -1.3419911674772 | -0.6788462093383 | 0 |
| 12 | 0.15336543775084 | 0.079786967797337 | 0 |
Table 3. The coefficients of FEoS (9).

| C_{i,j}  | 6   | 7   | 8   |
|---------|-----|-----|-----|
| i       | 0   | -0.047138797399686 | 0.14117088946202 | -0.075939444571892 |

The equation of state (9) represents experimental \( p, \rho, T \) data [12] within the range of the experimental error (figure~1). As in the case of the crossover equation of Tiesinga et al. [29], the deviations between the values calculated from equation (9) and the exact data of Gilgen et al. [12] remain within the range of 0.04% for densities from 400 to 650~kg/m\(^3\). The equation of state of Stewart and Jacobsen [30] does not represent these data with comparable uncertainty. Experimental data on \( C_v \) [26–28] in a wide range of state parameters, including the vicinity of the critical point, are transmitted within the experimental error range (figure~2).

![Relative deviations \( \delta p = \left( p_{\text{exp}} - p_{\text{cal}} \right) / p_{\text{exp}} \times 100\% \); \( p_{\text{cal}} \) corresponds to values calculated with the help of (9); \( p = p_{\text{exp}} \) are from data [12] over isothermal lines: 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.](image1)

![Relative deviations \( \delta C_v = \left( C_{v,\text{cal}} - C_{v,\text{exp}} \right) / C_{v,\text{exp}} \times 100\% \); \( C_{v,\text{cal}} \) corresponds to values calculated with a help of (9) or FEoS [2]; \( C_v = C_{v,\text{exp}} \) are from data [26–28] over isochoric lines: 1, 2–0.4736~g/cm\(^3\) [26]; 3, 4–0.531~g/cm\(^3\) [27]; 5, 6–0.531~g/cm\(^3\) [28]; 1, 3, 5–\( C_v = C_{v,\text{cal}} \) calculated with a help of the equation (9); 2, 4, 6–\( C_v = C_{v,\text{cal}} \) calculated with a help of the equation [2].](image2)
5. Conclusion
On the basis of the scaling hypothesis (3) the fundamental equation of state (9) has been developed. The equation operates satisfactorily in a wide range of pressures and temperatures including the critical region and this is the novelty.

In the regular part of the thermodynamic surface the FEoS possesses the properties of the virial series. In the critical region the FEoS possesses the properties of the Widom equation.

On the basis of FEoS we have developed the equation of state for argon (9), which satisfactorily conforms to the experimental data in a wide range of pressures and temperatures including the critical region. It is valid for temperatures from the saturation line and the melting line up to 2300–K and for pressures up to 2600–MPa.

References
[1] Ronchi C 1981 J. Nucl. Mater. 96 314–28
[2] Tegeler C, Span R and Wagner W 1999 J. Phys. Chem. Ref. Data 28 779–850
[3] Rizi A and Abbaci A 2012 J. Mol. Liq. 171 64–70
[4] Bezverkhyy P P and Martynets V G 2016 High Temp. - High Pressures 45 145–54
[5] Rykov V A 1985 J. Eng. Phys. Thermophys. 48 476–81
[6] Rykov V A 1985 J. Eng. Phys. Thermophys. 49 1502–8
[7] Kozlov A D, Lysenkov V F, Popov P V and Rykov V A 1992 J. Eng. Phys. Thermophys. 62 611–7
[8] Lysenkov V F, Kozlov A D, Popov P V and Yakovleva M V 1994 J. Eng. Phys. Thermophys. 66 286–94
[9] Rykov V A and Varfolomeeva G B 1985 J. Eng. Phys. Thermophys. 48 341–5
[10] Lysenkov V F and Rykov V A 1991 High Temp. 29 1236–8
[11] Ma Sh 1980 Sovremennaya Teoriya Kriticheskikh Yavleniy (Modern Theory of Critical Phenomena) (Moscow: Mir)
[12] Gilgen R, Kleinrahm R and Wagner W 1994 J. Chem. Thermodyn. 26 383–98
[13] Widom B 1965 J Chem. Phys. 43 255–62
[14] Voronel A V, Snigirev V G and Chaskin Yu A 1965 Sov. Phys. JETF 48 981–4
[15] Thoen J, Vangeel E and Van Dael W 1971 Physica 52 205–24
[16] Kudryavtseva I V and Rykov S V 2016 Russ. J. Phys. Chem. A 90 1493–5
[17] Rykov V A, Kudryavtseva I V, Rykov S V and Ustuzhanin E E 2018 J. Phys.: Conf. Ser. 946 012118
[18] Rykov V A, Rykov S V, Kudryavtseva I V and Sverdlov A V 2017 J. Phys.: Conf. Ser. 891 012334.
[19] Rykov V A, Kudryavtsev D A, Rykov S V and Rykov V A 2014 Scientific and Technical Bulletin of Povolzhie 2 44–7
[20] Rykov V A, Kudryavtsev D A and Rykov V A 2013 Scientific and Technical Bulletin of Povolzhie 5 50–3
[21] Altunin V V 1975 Teplofizicheskiye svoystva duvokisi ugleroda (Thermophysical properties of carbon dioxide) (Moscow: Standards Publishing)
[22] Klimock J, Kleinrahm R and Wagner W 1998 J. Chem. Thermodyn. 30 1571–88
[23] Gilgen R, Kleinrahm R and Wagner W 1994 J. Chem. Thermodyn. 26 399–413
[24] Michels A, Levelt J M and De Graaff W 1958 Physica 24 659–71
[25] Lecocq A. J. 1960 Rech. Centre Natl. Rech. Sci. Lab. Bellevue 11 55–82
[26] Stewart R B and Jacobsen R T 1989 J. Phys. Chem. Ref. Data 18 639–799
[27] Anisimov M A, Koval’chuk B A, Rabinovich V A and Smirnov V A 1978 Teplofizicheskiye svoystva veshchestv i materialov 12 86–106
[28] Anisimov M A, Koval’chuk B A, Rabinovich V A and Smirnov V A 1975 Teplofizicheskiye svoystva veshchestv i materialov 8 237–45
[29] Voronen’ A V, Gorbunova V G, Smirnov V A, Shmakov N G and Shchekochikhina V V 1973 Sov. Phys. JETF 36 505–13
[30] Tiesinga B W, Sakonidou E P and van den Berg H R 1994 J. Chem. Phys. 101 6944