Method for constructing fundamental equation of state based on the relationships of similarity theory and scaling hypothesis

Rykov S V\textsuperscript{1}, Kudryavtseva I V\textsuperscript{1}, Rykov V A\textsuperscript{1}

\textsuperscript{1} ITMO University, Kronvergskiy 49, Saint-Petersburg 197101, Russia

E-mail: togg1@yandex.ru

Abstract. On the basis of the new phenomenological theory of the critical point, the method for constructing fundamental equation of state (FEoS) of liquid and gas has been developed. Within the framework of the method proposed, a number of requirements are met: a) in the region of low densities, the transition of FEoS to the virial equation; b) in a wide vicinity of the critical point, the transition of FEoS to the Beres tov equation; c) taking into account asymmetry in the behavior of the isochoric heat capacity, isothermal compressibility coefficient and other thermodynamic functions relative to the critical isochore. To calculate the singular component of FEoS, the Pokrovsky transformations and the similarity relation connecting the parameters of a lattice gas and a real liquid are used. It has been shown that such an approach requires only knowledge of the density data on the saturation line and the values of the critical indices to calculate the singular component of FEoS. This allows us to exclude data on the isochoric heat capacity from the calculation scheme and recommend this method for constructing FEoS of substances little studied in the vicinity of the critical point.

The method has been tested on the example of constructing carbon dioxide FEoS. The workspace of FEoS has been set: by temperature \(216.592 \leq T \leq 1100\) K and by pressure up to 200 MPa. The results obtained are discussed.

1. Introduction

Currently, thermodynamic surface area directly adjacent to the critical point of the liquid still attracts the attention of many researchers [1–16]. To describe this part of the thermodynamic surface, the scaled equations of state [4–6], crossover equations [7–10] and fundamental equations of state (FEoS) [11–16] are used. And it is FEOs’s that have become the most widespread in recent years since the area of state parameters for the calculation of which equations [4–6] and [7–10] can be used is many times smaller both in pressure \(p\), and in temperature \(T\) than the one in fundamental equations of state [11–16] satisfying a number of requirements of the scaling theory (ST) [17]. For example, the workspace of the crossover equation [8] is in the temperature range of \(0.95 / 1.3 \leq T / T_c \leq 1.3\) and in FEoS [11] it is in the range of \(T_c / T_c \leq T / T_c \leq 9.1\). Here, \(T_c\) is the critical temperature.

In papers [1–3], new approaches to describing the critical point vicinity were discussed. In particular, in [3], a new representation of the scaling hypothesis was proposed. Within the framework of this representation, the asymmetry of a real fluid relative to the critical isochore was taken into account. In papers [14, 16] on the basis of [3], the equations of state of argon and R218 which satisfy all the power laws of ST fair for symmetric models were developed. In [18] it was shown that the representation of the scaling hypothesis proposed in [3] can be also extended to asymmetric systems in the vicinity of the critical point. A real fluid belongs to asymmetric systems [3]. We will use the
results of [18] in order to build FEoS that meets the requirements of ST and takes into account a real fluid features.

2. Construction method and structure of FEoS

According to [18], the Helmholtz free energy $F$ can be represented as:

$$F(\rho, T) = F_{ig}(T, \rho) + F_{reg}(\rho, T) + \phi(\omega) F_{nreg}(\rho, T),$$

(1)

where $F_{ig}(T, \rho)$ is the ideal gas component of $F$; $F_{reg}(\rho, T)$ and $\phi(\omega)$ are regular functions; $F_{nreg}(\rho, T)$ is the irregular function.

In accordance with recommendations of [18], we have presented the function $F_{nreg}(\rho, T)$ as a power series:

$$F_{nreg}(\rho, T) = R T Z \sum_{n=0}^{4} |\Delta \rho|^{\beta + \lambda} x^{n},$$

(2)

where $Z = \rho / (R T)$ is the critical compressibility; $R$ is the gas constant; $\Delta \rho = \omega - \rho / \rho_c$; $x = \tau / |\Delta \rho|^{\delta + \beta}$ is the scaling variable; $\tau = \frac{T}{T_c}$; $\Delta = \Delta_c$; $\lambda = 2 \beta - \alpha - \beta$; $\alpha$, $\beta$, $\delta$ and $\Delta$ are the critical indices; $\lambda = \Delta_c = \beta \delta - 1$.

The scaling functions $a_i(x)$ are calculated on the basis of the Scofield-Litster-Ho equation [19], the Berestov scaled equation [20], and the Kiselev crossover equation [21]. As a result, we have a number of functions $a_i(x)$ reduced to a dimensionless form:

$$a_0(x) = -\frac{u_i k_0 (\gamma + \lambda)}{2 \alpha \beta^{\gamma} \alpha_0 (1 - \epsilon)} \left[ (\phi + \phi_i)^{\gamma + \lambda} - \epsilon (\phi + \phi_2)^{\gamma + \lambda} \right] + \frac{u_i x_0^{\gamma + \lambda}}{2k} (\phi + \phi_3)^{\gamma + \lambda} + C_0,$$

(3)

$$a_i(x) = -\frac{u_i k_0 (\gamma + \lambda) x_0^{\gamma + \lambda}}{2 \alpha \beta^{\gamma} \alpha_0 (1 - \epsilon)} \left[ (\phi + \phi_i)^{\gamma + \lambda} - \epsilon (\phi + \phi_2)^{\gamma + \lambda} \right] + \frac{u_i x_0^{\gamma + \lambda}}{2k} (\phi + \phi_3)^{\gamma + \lambda} + C_1,$$

(4)

$$a_2(x) = u_i x_0^{\gamma + \lambda} \left[ (\phi + \phi_i)^{\gamma + \lambda} - \epsilon (\phi + \phi_2)^{\gamma + \lambda} + C_2 \right],$$

(5)

$$a_3(x) = u_i x_0^{\gamma + \lambda} \left[ (\phi + \phi_i)^{\gamma + \lambda} + C_3 \right],$$

(6)

$$a_4(x) = u_i x_0^{\gamma + \lambda} \left[ (\phi + \phi_i)^{\gamma + \lambda} - (\phi + \phi_3)^{\gamma + \lambda} + C_4 \right],$$

(7)

where $\epsilon = x_i / x_0$; $\alpha_i = (2 - \alpha + \Delta_i)(1 - \alpha - \Delta_i)$; $\gamma_i = (\gamma + \Delta_i)(\gamma + \Delta_i - 1)$; $u_p$ and $u_i$ are the individual parameters, $i \in \{1, 2, 3, 4\}$; $\phi = x / x_0$; $\phi_i = x_i / x_0$; $\epsilon \in \{1, 2, 3\}$; $x_0$ is the value of the scaling variable $x$ on the saturation line; $b^2 = (\gamma - 2 \beta)/[\gamma(1 - 2 \beta)]$; $k_0 = [(b^2 - 1) / x_0^3]$. We have found the coefficients $C_i$ from the equation: $(\delta + 1 + \lambda / \beta) a_i(\phi = -1) + (x_i / \beta) a_i(\phi = -1) = 0$.

We have chosen the function $F_{reg}(\rho, T)$ from the following conditions: (i) the FEoS should satisfy the requirement $p(\rho, T_c) = p_c$ where the values of the critical parameters $(p_c, \rho_c, T_c)$ are set from the processing of experimental data $(\rho^+, \rho^-, p_c)$ on the phase equilibrium line [22]; (ii) in the region of low densities, in the framework of the proposed approach, the thermal equation of state transforms into a virial equation. The function $F_{reg}(\rho, T)$ [16] satisfies these conditions:
Table 1. Coefficients $C_{ij}$ of FEoS (1).

| $i$ | 0 | 1 | 2 | 3 |
|-----|---|---|---|---|
| 0   | 0 | 0 | 2.0950664287226 | -1.9951562192948 |
| 1   | 0 | 0 | -1.696675665886 | 3.315393569871 |
| 2   | 0 | 0 | 3.799619416579 | -4.6319402086288 |
| 3   | 0 | -1.724247082806 | 1.1856458481539 | 0 |
| 4   | 0 | -1.2410343794484 | 6.831699945464 | 0.8787300822188 |
| 5   | 0 | 4.8974522665659 | 6.5475799847205 | -4.6109062875712 |
| 6   | -0.16292717913163 | -12.087692448882 | 3.1644090029594 | 5.138856663091 |
| 7   | 0.0365093215998 | 12.775762079764 | -8.862271892841 | -3.8769280860784 |
| 8   | 1.17223130967 | 0.2365803061317 | -0.022488579734529 | 2.8499253662385 |
| 9   | -1.8720094373382 | -16.286381687322 | 1.322747743617 | 1.76022721567 |
| 10  | 1.13835381387 | 17.196620933549 | -0.412159365726 | -0.2550799663569 |
| 11  | 0.5942939968107 | -2.5059017984143 | 0 | 0 |
| 12  | -1.5547126783082 | -4.950224351789 | 0 | 0 |
| 13  | 1.0209810746834 | 4.6869228460271 | 0 | 0 |
| 14  | -0.5700307414108 | -0.31180142611062 | 0 | 0 |
| 15  | -0.0073247053881338 | -1.529633794363 | 0 | 0 |
| 16  | -0.1348291268229 | 0.71622903730829 | 0 | 0 |
| 17  | 0.0469689533423 | -0.16882001485554 | 0 | 0 |
| 18  | -0.0054856973556425 | 0.016543845892616 | 0 | 0 |

Table 2. Coefficients $C_{ij}$ of FEoS (1).

| $i$ | 4 | 5 | 6 | 7 |
|-----|---|---|---|---|
| 0   | 3.9502706687144 | 12.700588434285 | 16.08111535862 | -8.5071359123969 |
| 1   | -1.4628004870318 | -7.015367555561 | -5.7752122406657 | 10.99529025106 |
| 2   | -4.3442963543527 | -9.4339196755545 | 0 | 0 |
| 3   | 0 | 0 | 0 | 0 |
| 4   | 5.7802951741598 | 1.1162749652843 | 0 | 0 |
| 5   | -0.073697340644565 | 0.89260157445282 | 0 | 0 |
| 6   | -4.6592278163644 | 0 | 0 | 0 |
| 7   | 6.6659187940551 | 0 | 0 | 0 |
| 8   | -4.2202468780455 | 0 | 0 | 0 |
| 9   | 0.82011755180161 | 0 | 0 | 0 |

\[
F_{\text{reg}}(\rho, T) = RT\omega y_z + RT\omega (Z_c - 0.2) y_x + RT\omega \tau_i \left[ D_1 (\omega - 3) + D_2 (\omega^2 - 2\omega) \right] + RT\omega D_3 (y_z - y_e) + RT\omega \sum_{i=0}^{N} \sum_{j=0}^{M} \left( C_{i,j} \tau' \Delta \rho' \right). 
\]

(8)

where \( \tau_i = \tau_i^1 \); \( y_z = 7.7 / 6 + 2.9 / 6\Delta \rho - 1.1 / 6\Delta \rho^3 + 0.05\Delta \rho^3 \); \( y_x = 5 - 4\Delta \rho + 3\Delta \rho^3 - 2\Delta \rho^3 + \Delta \rho^4 \); \( y_z = 0 \). 

FEoS (1) with components (2) and (8) meets the requirements:
\[ \left( \frac{\partial^n p}{\partial \rho^n} \right)_T = 0 \text{ and } \left. \left( \frac{\partial p}{\partial \rho} \right)_{T = \tau, \rho = \rho_c} \right|_{T = 0} = o(\tau), \]  
\tag{9}

Where \( n \in \{1, 2, 3, 4\} \); and \( o \) is the Landau symbol [23].

In addition, the function \( \phi_0(\omega) \) is chosen to meet the following conditions:

\[ \phi_0(\omega \rightarrow 0) \equiv o(\omega^2), \]  
\tag{10}

\[ \phi_0(\omega \rightarrow 1) \rightarrow \text{const} + o((\Delta \rho)^3) \]  
\tag{11}

As a result, we used the following function \( \phi_0(\omega) : \phi_0(\omega) = (\Delta \omega)^3 - 1 \).

Fulfillment of requirement (10) provides a qualitatively correct description of the region of low densities and pressures on the basis of \( F^{\text{reg}}(\rho, T) \), and fulfillment of requirements (9) and (11) allows reproducing the power laws of ST on the basis of \( F^{\text{reg}}(\rho, T) \), since in this case FEoS (1) comes to the Widom scaled equation in the asymptotic vicinity of the critical point [3].

### 3. Testing the proposed method on the construction example of carbon dioxide FEoS

When constructing the carbon dioxide FEoS, the results of [24] were used. There, the relation of similarity between the parameters \( k_0 \) and \( u_0 \) of the lattice gas model (symmetric model) and the parameters \( k_p \) and \( u_p \) of a real fluid (asymmetric model) was established:

\[ k_p = k_0 (1 - uv)^{\beta} \text{ and } u_p = u_0 (1 - uv)^{\beta \delta}, \]  
\tag{12}

where \( u \) and \( v \) are the constants of the Pokrovsky transformations [25].

The equality directly follows from (12):

\[ k_p u_p^{-1/\delta} = k_0 u_0^{-1/\delta}. \]  
\tag{13}

The authors of [24] showed that the following dependence took place:

\[ k_p u_p^{-1/\delta} = A + BZ_c, \]  
\tag{14}

where \( A \) and \( B \) are the constants.

In accordance with [26], we have accepted \( u = 0 \) and obtained the required dependence for the parameter \( u_p \):

\[ u_p = \left[ k_p \right]^{\delta} = \left[ k_0 (1 - uv)^{\beta} / (A + BZ_c) \right]^{\delta} \]  
\tag{15}

where \( A = 1.2687470329251 \) and \( B = -2.2988501100973 \). We have obtained these values by processing the graphic information given in [24]. Note that the dependence (15) with the given values \( A \) and \( B \) leads to good results if the critical indices satisfy the conditions: \( \alpha \equiv 0.11 \) and \( \delta \equiv 4.8 \).

We have found the value of the parameter \( x_0 \) that is included in \( k_0 \) as a result of data processing [22] on the carbon dioxide saturation line based on the method [27]: \( x_0 = 0.2356029152870178 \).

We will take the values of the critical indices in accordance with the ST [17]: \( \beta = 0.325 \) and \( \gamma = 1.24 \). In this case, \( \Phi_1 = 2.80724769, \Phi_2 = 14.4717304, \Phi_3 = 5.73246825 \) [16]. Thus, we have found all the parameters and coefficients of the scaling function (5), which determines the behavior nature of \( C_q \), \( K_r \) and other thermodynamic functions in the asymptotic vicinity of the critical point. We have chosen the function \( F_{ig}(T, \rho) \) in accordance with the recommendations of [28].
The remaining parameters and coefficients of FEoS (1)–(8) have been set on the basis of the data of [22, 29–37]: \( T_c = 304.1282 \text{ K}; \) \( p_c = 73.77298 \text{ bar}; \) \( \rho_c = 467.6001 \text{ kg/m}^3; \) \( R = 1.8892405 \text{ J/(g K)}; \) \( u_0 = 4.647724785682; \) \( u_i = -4.21548189625; \) \( u_j = -2.49322174794\times10^{-4}; \) \( u_3 = 0.012635019738; \) \( c_T = 304.1282; \) \( c_p = 73.77298; \) \( c_\rho = 467.6001; \) \( R_0 = 1.8892405 \text{ J/(g K)}; \) \( u_4 = 4.647724785682; \) \( u_1 = -4.21548189625; \) \( u_2 = -2.49322174794\times10^{-4}; \) \( u_3 = 0.012635019738; \) \( D_1 = 0.74828177414; \) \( D_2 = 0.92408900081; \) \( D_3 = 3.33477022226\times10^{-3}; \) and \( \alpha = 0.11; \) \( \delta = 4.815; \) \( \Delta = 0.51. \) The values of the coefficients \( C_{ij} \) are given in tables 1, 2.

In order to estimate the uncertainties of \( (\rho - \rho_c)/\rho \times 100\% \) and \( (p - p_c)/p_c \times 100\% \) with which FEoS describes the values \( \rho, p \) and \( C_V \) both in the single-phase region, and on the saturation line, we have calculated the AAD by the density \( A_\rho, \) the pressure \( A_p, \) and the isochoric heat capacity \( A_{C_V}. \) As a result, we have obtained the following AAD values for experimental and calculated data [28–41]: \( A_\rho = 0.0785\% \) and \( A_p = 0.147\% \) [33], \( A_\rho = 0.237\% \) and \( A_p = 0.250\% \) [29–32], \( A_\rho = 0.078\% \) and \( A_p = 0.078\% \) [34], \( A_\rho = 0.139\% \) and \( A_p = 0.39\% \) [36], \( A_\rho = 0.2049\% \) and \( A_p = 0.267\% \) [35], \( A_\rho = 0.0718\% \) and \( A_p = 0.1171\% \) [28], \( A_\rho = 0.3124\% \) and \( A_p = 0.293\% \) [22], \( A_\rho = 0.131\% \) and \( A_p = 0.0284\% \) [22], \( A_\rho = 0.136\% \) and \( A_p = 0.0667\% \) and \( A_\rho = 0.0870\% \) [28], \( A_{C_V} = 2.53\% \) [38], \( A_{C_V} = 4.52\% \) [39], \( A_{C_V} = 6.22\% \) [40], and \( A_{C_V} = 4.66\% \) [41].

When describing the isochoric heat capacity of FEoS (1), we have taken into account that the critical temperatures of \( \text{CO}_2 \) corresponding to the given experimental data on \( C_V \) are significantly overestimated compared to the value \( T_c \) used in this paper. Therefore, we have corrected the temperatures given in [39], [40] and [41] to \( \Delta T = 0.02 \text{ K}, \) \( \Delta T = 0.005 \text{ K} \) and \( \Delta T = 0.0222 \text{ K}, \) respectively.

### 4. Summary

Using the example of describing equilibrium properties of \( \text{CO}_2, \) we have shown that the new representation of the scaling hypothesis [18] allows constructing the FEoS which in the gas region has properties of the virial type equation, and in the vicinity of the critical point takes into account the features of a real liquid in accordance with ST. It has been shown that to calculate the singular component of FEoS, one can use only the density data on the saturation line and the values of critical indices. The boundaries of the workspace of FEoS (1) of carbon dioxide have been determined to be \( 216.592 \leq T \leq 1100 \text{ K} \) and \( p \leq 200 \text{ MPa}. \)

### 5. Conclusion

In our view, the method of constructing FEoS (1) which takes into account the behavior peculiarities of a real fluid in a wide vicinity of the critical point can be recommended for constructing equations of state for both pure substances for which there exist reliable data on \( C_V \) in the vicinity of the critical point, and substances for which such data are not available.

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