Method of constructing a fundamental equation of state based on a scaling hypothesis

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Abstract. The work studies the issues associated with the construction of the equation of state (EOS) taking due account of substance behavior in the critical region and associated with the scaling theory of critical phenomena (ST). The authors have developed a new version of the scaling hypothesis; this approach uses the following: a) substance equation of state having a form of a Schofield-Litster-Ho linear model (LM) and b) the Benedek hypothesis. The Benedek hypothesis has found a similar behavior character for a number of properties (isochoric and isobaric heat capacities, isothermal compressibility coefficient) at critical and near-critical isochors in the vicinity of the critical point. A method is proposed to build the fundamental equation of state (FEOS) which satisfies the ST power laws. The FEOS building method is verified by building the equation of state for argon within the state parameters range: up to 1000 MPa in terms of pressure, and from 83.056 К to 13000 К in terms of temperature. The executed comparison with the fundamental equations of state of Stewart-Jacobsen (1989), of Kozlov at al (1996), of Tegeler-Span-Wagner (1999), of has shown that the FEOS describes the known experimental data with an essentially lower error.

1. Introduction

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The problem of building up the fundamental equation of state (FEOS) taking due account of the peculiarities of substance behavior in the field of critical states draws attention of many researchers [1–6]. We have analyzed various known approaches within the framework of which there has been achieved greatest success including the consideration of the results of works [1, 2] where there have been developed crossover equations of state written down in parametric form; such an equation goes over to the Schofield-Litster-Ho equation of state [7]:

Our analysis demonstrates that the crossover equations [1, 2] have a working region which is limited by the following parameters $0.4 \leq \omega \leq 1.3$ and $0.97 \leq t \leq 1.3$ ($\omega = \rho / \rho_c$, $t = T / T_c$).

The authors [4] have proposed to solve the problem of building up the fundamental equation of state (FEOS) on the basis of a combined equation having an empirical form:

$$p(p, T) = p_c(p, T) + \phi_t(p, T)p_t(p, T),$$

(1)
where $p_r(\rho,T)$ – regular function; $p_n(\rho,T)$ – irregular component of the equation (1).

The authors [4] have attracted the Landau function [8] as a function of $\phi_c(\rho,T)$. Our analysis leads to the conclusion that the equation of state (1) considered in [4] has a number of drawbacks. First of all, in order to qualitatively truly convey the behavior of the critical isotherm and the isothermal compressibility coefficient, it is necessary to perform the following relations for the following derivatives [9]:

$$
\left( \frac{\partial p^n}{\partial \rho^n} \right)_{T=\bar{T}, \rho=\bar{\rho}_1} = 0 \quad \text{and} \quad \left( \frac{\partial p^i}{\partial \rho^i} \right)_{T=\bar{T}, \rho=\bar{\rho}_1} = o(\tau),
$$

where $n \in \{1,2,3,4\}$, $\rho_c$ and $T_c$ – critical parameters, $o$ – Landau symbol.

Within the framework of the approach [4], only two equations out of the conditions (2) are accomplished, namely

$$
\left( \frac{\partial p^i}{\partial \rho^i} \right)_{T=\bar{T}, \rho=\bar{\rho}_1} = 0
$$

and

$$
\left( \frac{\partial p^i}{\partial \rho^i} \right)_{T=\bar{T}, \rho=\bar{\rho}_1} = 0.
$$

In the second instance, we have performed numerical evaluation of complementary functions, among them the scaling function $h_m(x)$ relating to the chemical potential $\mu$, and the scaling function $f_m(x)$ relating to the isochoric heat capacity $C_v$ which are linked with the equation of state (1) [4]. Similar calculations have been performed for the specified complementary functions relating to the Schofield linear model [7]. The comparison has detected an essential deviation between the specified functions. For example, the deviation of the scaling function $f_m(x)$ relating to the equation (1) from the scaling function of the isochoric heat capacity $f_m(x)$ relating to the Schofield linear model [7] has reached 26% [10].

In the third instance, the thermal equation of state (1) [4] and the pertinent calculation formulae relating to the properties (Helmholtz’s free energy $F$, isochoric heat capacity $C_v$, isobaric heat capacity $C_p$) contain differential binomial integrals. These nontrivial mathematical aspects do essentially hamper the calculation of the specified thermodynamic properties.

In order to build a single equation of state, the works [5, 6] make use of the Helmholtz free energy $F(\rho,T)$: in this approach the authors used certain ST requirements. Along with this, the authors have attracted the «method of pseudocritical points» [11]. It should be noted that this equation of state has an empirical form, just as the equation of state proposed in [4].

2. Derivation of the fundamental equation of state on the basis of new presentation of the scaling hypothesis

The study [12] considers a new version of the scaling hypothesis; in this approach the following is used substance equation of state having a form of a Schofield-Litster-Ho linear model (LM) and the Benedek hypothesis [13]. This work plans to use a new version of the scaling hypothesis and to develop a fundamental equation of state (FEOS) which meets the following conditions:

a) it should not be inferior in terms of accuracy to the virial equations of state when describing the regular part of thermodynamic surface,

b) it should meet the ST main requirements [14] when describing the properties in the broad neighborhood of the critical point.

The proposed method of FEOS building is based on the representation of the scaling hypothesis in the following form [12]:

$$
\Delta S \times X^{\frac{1-\alpha}{\tau}} = \varphi_0 + \varphi_2 m^2, \quad m = \Delta \rho \times X^\beta,
$$

(3)
where  \( \Delta S = \left( \rho T_v / \rho_v \right) [S(\rho, T) - S_0(T)] / \phi(\omega) \) – reduced entropy;  \( S_0(T) \) and  \( \phi(\omega) \) – regular functions;  \( \rho_v \) – critical pressure;  \( \Delta \rho = \omega - 1 \);  \( \omega = \rho / \rho_v \);  \( \alpha, \beta, \chi \) – critical indices;  \( X \) – thermodynamic function which is characterized by a critical index  \( \chi \) (for instance,  \( X = X_1 = C_v \) and  \( \chi = \chi_1 = \alpha \),  \( X = X_2 = K_v \) and  \( \chi = \chi_2 = \gamma \)).

For the version  \( X = X_1 = C_v \), the equation (3) may be derived directly from the Schofield linear model (LM) [7]. Let us plug the components ( \( X = X_1 = C_v \) and  \( \chi = \chi_1 = \alpha \),  \( X = X_2 = K_v \) and  \( \chi = \chi_2 = \gamma \),  \( X = X_3 = C_p \) and  \( \chi = \chi_3 = \gamma \)) successively into (3). As a consequence, we obtain the following expression for the function of  \( \Delta S \):

\[
\Delta S = \sum_{i=1}^{3} A_i' \left| \Delta \rho \right|^{1-\alpha_i} \left| x + x_i \right|^{\alpha_i-1} + B_i' \left| \Delta \rho \right|^{1-\beta_i} \left| x + x_i \right|^{\beta_i-1},
\]

where  \( A_i' = \left( D_i \right)^{(\alpha_i-1)/\gamma_i} \);  \( B_i' = \left( D_i \right)^{(1-\gamma_i)/\gamma_i}, \quad i \in \{1,2,3\} \).

Let us express function  \( S \) by using (4) and plug it into the known thermodynamic relationship  \( F = -\int S \, dT \). As a consequence, a fundamental equation of state is obtained in the form:

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

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

The component  \( F_{\text{irreg}}(\rho, T) \) has a form:

\[
F_{\text{irreg}}(\rho, T) = \frac{P}{\rho_v} \phi_0(\omega) \left| \Delta \rho \right|^{\phi+1} a(x),
\]

Here  \( a(x) \) – the Helmholtz free energy scaling function:

\[
a(x) = \sum_{i=1}^{3} \left( A_i' (x + x_i)^{2-\alpha} + B_i' (x + x_i)^{\gamma} \right) + C,
\]

where  \( A_i = A_i' / (\alpha - 2) \);  \( B_i = -B_i' / \gamma; \quad i \in \{1,2,3\} \);  \( C = C_1 + C_2 + C_3; \quad C_1, \quad C_2, \quad C_3 \) – constants of integration.

Our analysis showed that the calculated characteristics of equation (5) can be improved in the case of argon if the component  \( F_{\text{irreg}}(\rho, T) \) has a form:

\[
F_{\text{irreg}}(\rho, T) = \frac{P}{\rho_v} \phi(\omega, \tau) \left| \Delta \rho \right|^{\phi+1} a(x),
\]

where  \( \phi(\omega, \tau) = \phi_0(\omega) / \tau^3; \quad \phi_0(\omega) = \left[ (\Delta \omega)^2 - 1 \right]^2 \).

3. Fundamental equation of state for argon

The evaluation of the fundamental equation of state (FEOS) proposed in the work will be conducted through the example of describing the equilibrium properties of argon. The selection of argon is largely driven by that it is referred to a group of substances well studied in terms of thermodynamics, both in the regular part of thermodynamic surface and in the vicinity of the critical point [15–30].

With due account of the conditions (2), the FEOS (5) has been reduced to the following form:
\[ F(\rho, T) = F^o(T, \rho) + RT \omega y_2 + RT \omega (Z_e - 0.2) y_6 \\
+ RT \omega \tau_i \left[ D_i (\omega - 3) + D_2 (\omega^2 - 2\omega) \right] + RT \omega D_i (y_4 - y_6) \\
+ RT \omega \sum_{j=0}^{14} \sum_{j=0}^{3} \left( C_{ij} \tau_i^j \Delta \rho^j \right) + RT \phi_0 (\omega) \phi_1 (t) |\Delta \rho|^{\beta} a_9 (x), \]

where \( F^o(T, \rho) \) – ideal gas component of argon free energy: [15]:

\[ F^o(T, \rho) = RT \left( \ln \omega + a_i^o + a_i^o t^{-1} - 1.5 \ln t \right). \tag{10} \]

with \( a_i^o = 58.316 \ 662 \ 43 \) and \( a_6^o = 524.946 \ 511 \ 64 \).

Here functions \( y_2, y_4, y_6 \) have the following form:

\[ y_2 = 7.7 / 6 + 2.9 / 6 \Delta \rho - 1.1 / 6 \Delta \rho^2 + 0.05 \Delta \rho^3, \quad y_4 = 5 - 4 \Delta \rho + 3 \Delta \rho^2 - 2 \Delta \rho^3 + \Delta \rho^4, \]
\[ y_6 = 4 - 3 \Delta \rho + 2 \Delta \rho^2 - \Delta \rho^3 + \Delta \rho^4. \]

The thermal equation and heat capacity of \( C_v \) obtained on the basis of dependencies (9), (10) and condition \( p(\rho, T) = p_c \) are presented in the following form:

\[ Z(\rho, T) = 1 + y_2 \omega^2 + y_4 \omega + D_3 \left( y_2 \omega^2 + y_4 \omega - y_6 \omega^2 - y_6 \omega \right) + \left( y_4 \omega^2 + y_6 \omega \right) (Z_e - 0.2) \\
+ \omega \sum_{i=0}^{14} \sum_{j=0}^{3} C_{ij} \tau_i^j \Delta \rho^{j+1} (i \omega + \Delta \rho) + D_5 \omega \tau_i (2 \omega - 3) + D_6 \omega^2 \tau_i (3 \omega - 4) \tag{11} \\
+ D_7 \omega |\Delta \rho|^3 \phi_1 (t) \phi_0 (\omega) \text{sign}(\Delta \rho) \left( (\delta + 1) a(x) - \frac{\chi}{\beta} a'(x) \right) + \phi_0 (\omega) |\Delta \rho| a(x), \]

\[ C_i = -R \omega^2 \sum_{i=0}^{14} \sum_{j=0}^{3} C_{ij} (j - 1) \tau_i^{j-2} \Delta \rho^{j-1} - 1.5 R \\
- R \omega |\Delta \rho|^{\beta} \left[ a_i^o (x) \phi_1 (t) + 2 |\Delta \rho|^{\beta} a_i^o (x) \phi_1 (t) + |\Delta \rho|^{2\beta} \phi_1 (t) a_9 (x) \right], \tag{12} \]

where \( y_1 = y_2' (\omega), \ y_3 = y_4' (\omega), \ y_5 = y_6' (\omega). \)

The coefficients and parameters of FEOS (9) have been calculated on the basis of the array of experimental data [16–30]. As a consequence, there have been obtained the following values for the coefficients \( (D_i) \) and other parameters (9): \( T_c = 150.66 \text{ K}; \ p_c = 48.634 \text{ MPa}; \ \rho_c = 535.1 \text{ kg/m}^3; \)
\( R = 208.13332 \text{ J/(K \times mol)}; \ \alpha = 0.11; \ \gamma = 1.24; \ D_5 = 4.179; \ D_6 = 0.5189933835608; \)
\( D_7 = 0.89853870299103; \ D_i = -2.7819037020431 \times 10^{-3}. \)

The values of coefficients \( C_{ij} \) are presented in tables 1 and 2.

| \( i \) | \( j \) | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|
| 0 | 0 | 0 | 2.421016075 | 3.764103684 | 0.923327725 |
| 1 | 0 | 0 | -1.994989141 | -2.705679411 | 0.211126833 |
| 2 | 0 | 0 | -4.227960595 | -11.90340871 | -9.855160937 |
| 3 | 0 | -1.477153275 | 3.199628429 | 10.88973974 | 8.322508341 |
| 4 | 0 | 0.865155311 | 8.797284663 | 20.02632309 | 16.7889711 |
| 5 | 0 | -0.020844175 | -10.60159548 | -28.57084452 | -23.71936186 |
Table 2. Coefficients \( (C_{ij}) \) of FEOS (9).

| \( i \) | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|
| 0 | 0.018161867 | 0.049644831 | 0.050920909 | -0.13592459 | 0.066061329 |
| 1 | 0.572652901 | 0.010342971 | 0 | 0 | 0 |
| 2 | -3.126567059 | -0.008647162 | 0 | 0 | 0 |
| 3 | 2.021415505 | 0 | 0 | 0 | 0 |
| 4 | 4.454159418 | 0 | 0 | 0 | 0 |
| 5 | -5.403773958 | 0 | 0 | 0 | 0 |
| 6 | -0.121226468 | 0 | 0 | 0 | 0 |
| 7 | 2.67520938 | 0 | 0 | 0 | 0 |
| 8 | -1.349247917 | 0 | 0 | 0 | 0 |
| 9 | 0.210151266 | 0 | 0 | 0 | 0 |

The fundamental equation of state (9) represents experimental \( p - \rho - T \) data \[17\] within the range of the experimental error (figure 1). The experimental data on \( C_v \) \[26, 30\] in the broad neighborhood of the critical point are transmitted within the experimental error range (figure 2). Hereby the equation of state (9) qualitatively truly reproduces the behavior of \( C_v \) in this field of state parameters.
Figure 1. Relative density deviations of argon in a single-phase region computed as per the equation (11) from the data [17], [20] over isothermal lines: 1 – 150.621 K [17]; 2 – 150.579 K [17]; 3 – 150.52 K [17]; 4 – 150.372 K [17]; 5 – 149.983 K [17]; 6 – 150.65 K [20].

Figure 2. Behavior of the isochoric heat capacity of argon in a single-phase region over the isochor of 531 kg/m$^3$. 1 – experimental points [30]; 2 – experimental points [26]; 3 – calculation as per the equation (12).

4. Conclusion
A new version of the scaling hypothesis (3) is developed; in this approach we have used: a) substance equation of state having a form of a Schofield-Litster-Ho linear model and b) the Benedek hypothesis. On the basis of the scaling hypothesis (3) there has been developed a fundamental equation of state (9) which firstly satisfactorily operates in a wide range of pressures and temperatures including the critical region. In the second instance, in the regular part of the thermodynamic surface the FEOS possesses
the properties of the virial series [31]. In the third instance, in the critical region the FEOS possesses the properties of the Widom equation.

On the basis of FEOS there has been developed an equation of state for argon (9), R1234yf, R707 which satisfactorily conforms to the experimental data in a wide range of pressures and temperatures including the critical region.

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