

# Universal Crossover Approach to Equation of State for Fluids

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It is well known that any classical equation of state fails to describe the properties of fluids in the critical region, where the behavior of fluids is strongly affected by density fluctuations. In the present work, a universal approach to incorporate the effects of density fluctuations in the global behavior of one-component fluids is proposed. As an illustration of our general approach, a crossover generalization of a four-parametric cubic equation of state, which can be useful for engineering applications, is demonstrated. The obtained crossover equation reproduces Ising-like singular scaling behavior in the critical region and reduces to the original cubic equation of state far away from the critical point. In addition, the crossover equation of state is applied to describe thermodynamic properties of methane, ethane, carbon dioxide, and water. It is shown that incorporation of critical fluctuations leads to a significant improvement in the ability of the cubic equation to represent thermodynamic properties and liquid–vapor equilibrium of one-component fluids.

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**KEY WORDS:** coexistence curve; critical point; equation of state; one-component fluids; thermodynamic properties.

## 1. INTRODUCTION

Traditionally, for the description of thermodynamic properties of one-component fluids in a wide range of pressures and temperatures, one uses various modifications of cubic equations of state [1, 2]. In this paper any equations of this type will be called mean-field equations of state. The application of these mean-field equations encounters a fundamental

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problem, which is associated with the singular behavior of thermodynamic properties of fluids in the critical region. It is well known that singular behavior of fluids in the critical region is caused by anomalous density fluctuations. Another effect of the critical fluctuations is a shift of critical parameters. Thus, the fluctuation effects inevitably make a mean-field equation of state useless in the critical region. In particular, system-dependent coefficients in the mean-field equations correlate with the mean-field values of the critical temperature  $T_0$ , pressure  $P_0$ , and density  $\rho_0$ , which do not coincide with the actual experimental values  $T_c$ ,  $P_c$ , and  $\rho_c$ .

Equations of state, which incorporate the fluctuation effects in the critical region and reduce to mean-field equations far from the critical point, are called the crossover equations of state. Crossover generalizations of various mean-field equations of state have been presented in a number of recent publications (see, for example, [3–6]). In all these works a general approach to obtain crossover equations of state is similar and can be represented by a set of consecutive operations. A mean-field equation of state and an appropriate thermodynamic potential are selected. A so-called singular part of the thermodynamic potential is separated from a regular background. The critical part is formulated in terms of dimensionless deviations of the thermodynamic variables from their critical values. The principal requirement for the critical part means a possibility to represent it in the form of an analytical Landau expansion (if the critical fluctuations are neglected) [7]. Finally, the actual (crossover) critical part of the thermodynamic potential, affected by fluctuations, is obtained by scaling renormalization of the dimensionless thermodynamic variables in the Landau-expansion critical part. The principal defect of this approach is the following. The scaling transformations are not applicable to any physical variable, but only to variables that possess a definite scaling dimensionality. These variables are called the scaling variables. Thus, the main problem in the crossover procedure can be formulated as a definition of scaling variables and their relations with experimental physical variables.

In the present paper four sets of physical variables are considered, namely, scaling mean-field and crossover variables and experimentally controlled thermodynamic mean-field and crossover variables. A general approach to formulate the crossover equation of state is proposed. Within this approach the relations between the different sets of physical variables are postulated. In particular, relations between the experimental variables and the scaling ones enable us to obtain a crossover equation of state by a conventional fluctuation-induced renormalization of the scaling variables. It should be taken into account that a fluctuation shift of the critical point also leads to a change in relations between the mean-field thermodynamic variables and the variables controlled by experimental conditions in real

fluids. In other words, the relations between the mean-field and crossover thermodynamic variables define the shifts of the critical parameters.

## 2. SCALING VARIABLES

In accordance with scaling theory [8], a Helmholtz-like potential  $F$  is a function of some scaling variables in the critical region. These variables characterize changes of the system symmetry at the phase transition. For the potential  $F$  such variables are the order parameter  $\varphi_1$  and the temperature-like field  $h_2$  [8]. Let us also define a field-dependent Gibbs-like thermodynamic potential  $\Phi$  which depends on the temperature-like field  $h_2$  and the ordering field  $h_1$  thermodynamically conjugated to the order parameter:

$$\Phi(h_2, h_1) = F(h_2, \varphi_1) - h_1 \varphi_1. \quad (1)$$

For the potentials  $F$  and  $\Phi$  the following differential relations take place:

$$dF = -\varphi_2 dh_2 + h_1 d\varphi_1, \quad d\Phi = -\varphi_2 dh_2 - \varphi_1 dh_1, \quad (2)$$

where  $\varphi_2$  is the scaling analog of the entropy. Furthermore, the functions  $F$  and  $\Phi$  will be called the scaling potentials in contrast to traditional thermodynamic potentials, which depend on experimental thermodynamic variables.

To obtain a crossover equation of state, it is necessary to define relations between the scaling and experimental thermodynamic variables. In the present work, for this purpose, we formulate relations between the scaling potentials  $F$  and  $\Phi$  and the Helmholtz energy  $A$  and Gibbs energy  $G$ , which depend on experimental thermodynamic variables. At first, the relations between the scaling and thermodynamic potentials are defined in the mean-field approximation. Secondly, a generalization for the fluctuation region is performed by corresponding renormalization of the scaling variables.

In the mean-field approximation the scaling potentials are given by the Landau theory:

$$F_m = u_2 h_{2m} \varphi_{1m}^2 + u_4 \varphi_{1m}^4, \quad \Phi_m = F_m - h_{1m} \varphi_{1m}. \quad (3)$$

Here and below, the thermodynamic quantities in the mean-field approximation are marked by the index "m". In this work the molar density of the Helmholtz energy and the Gibbs energy are used as the thermodynamic potentials. We note that the mean-field equation of state is supposed to be known and, consequently, an explicit form of the thermodynamic potentials  $A_m$  and  $G_m$  is also known.

### 3. SINGULAR PARTS OF THE THERMODYNAMIC POTENTIALS

Now we define dimensionless thermodynamic quantities in the mean-field approximation.  $\bar{P}_m = P_m/P_0$  is the dimensionless pressure,  $\bar{A}_m = A_m/RT_0$  is the molar free-energy,  $\bar{G}_m = G_m/RT_0$  is the molar Gibbs energy,  $\bar{T}_m = T_m/T_0$  and  $\bar{v}_m = v_m z_0/v_0$  are the reduced temperature and molar volume, respectively,  $z_0 = P_0 v_0/RT_0$  is the critical compressibility factor in the mean-field approximation, and  $R$  is the universal molar gas constant. Obviously, the final results do not depend on a particular normalization. Therefore, the dimensionless quantities are selected just for convenience. As will be clear below, the inclusion of the critical compressibility factor into the expression for the dimensionless molar volume facilitates the analysis of the initial cubic equation of state. Besides, henceforward the experimental values of the critical parameters  $T_c$ ,  $P_c$ , and  $v_c$  will be used to define the dimensionless crossover quantities.

The differential relations for the dimensionless molar thermodynamic potentials  $\bar{A}_m$  and  $\bar{G}_m$  can be written in the form,

$$d\bar{A}_m = -\bar{s}_m d\bar{T}_m - \bar{P}_m d\bar{v}_m, \quad d\bar{G}_m = -\bar{s}_m d\bar{T}_m + \bar{v}_m d\bar{P}_m, \quad (4)$$

where  $\bar{s}_m = s_m/R$  is the dimensionless molar entropy in the mean-field approximation. Let us define the critical part of the molar Helmholtz energy, which reproduces the Landau expansion near the mean-field critical point and becomes singular near the actual critical point affected by fluctuations. For this purpose one defines the ordering field in the system

$$\Delta\bar{P}_m = \bar{P}_m - \bar{P}_s^m, \quad (5)$$

where

$$\bar{P}_s^m(\bar{T}_m) = \begin{cases} \bar{P}_m(\bar{T}_m, \bar{v}_0), & \text{if } \bar{T}_m > 1 \\ \bar{P}_m(\bar{T}_m, \bar{v}_m^1), & \text{if } \bar{T}_m \leq 1 \end{cases}, \quad (6)$$

and  $\bar{v}_m^1$  is the molar volume of the liquid phase.

Now let us define the singular part of the molar free energy by the condition,

$$\left( \frac{\partial \bar{A}_s^m}{\partial \bar{v}_m} \right)_{\bar{T}_m} = -\Delta\bar{P}_m. \quad (7)$$

Integrating this equation one finds

$$\bar{A}_s^m = \bar{A}_m - \bar{A}_0^m - \Delta\bar{v}_m \bar{P}_s^m, \quad (8)$$

where  $\bar{A}_m = - \int \bar{P}_m d\bar{v}_m$  is the molar Helmholtz energy,  $\bar{A}_0^m = \bar{A}_m(\bar{T}_m, \bar{v}_0)$ , and  $\Delta\bar{v}_m = \bar{v}_0 - \bar{v}_m$  is the dimensionless deviation of the molar volume from its critical value. In this case the coexistence curve is determined by two conditions:

$$\left( \frac{\partial \bar{A}_s^m}{\partial \Delta\bar{v}_m} \right)_{\bar{T}_m} = \Delta\bar{P}_m = 0, \quad \bar{A}_s^m(\Delta\bar{v}_m^l) = \bar{A}_s^m(\Delta\bar{v}_m^g), \quad (9)$$

The first one coincides with the condition,  $\bar{P}_m(\bar{v}_m^l) = \bar{P}_m(\bar{v}_m^g)$  and the second one coincides with the condition of equal chemical potentials in the coexisting phases.

Let us also define the singular part of the molar Gibbs potential (known as the chemical potential) connecting it with the singular part of the free-energy density  $\bar{A}_s^m$  by a common Legendre transformation;

$$\bar{G}_s^m = \bar{A}_s^m - \Delta\bar{v}_m \Delta\bar{P}_m. \quad (10)$$

Within these definitions for the quantities  $\bar{A}_s^m$  and  $\bar{G}_s^m$ , the following differential relations take place:

$$\begin{aligned} d\bar{A}_s^m &= - \left( \Delta\bar{s}_m + \Delta\bar{v}_m \left( \frac{d\bar{P}_s^m}{d\bar{T}_m} \right) \right) d\bar{T}_m + \Delta\bar{P}_m d\Delta\bar{v}_m, \\ d\bar{G}_s^m &= -\Delta\bar{s}_m d\bar{T}_m - \Delta\bar{v}_m d\bar{P}_m, \end{aligned} \quad (11)$$

where  $\Delta\bar{s}_m = \bar{s}_m - \bar{s}_0^m$  and  $\bar{s}_0^m = - (d\bar{A}_0^m/d\bar{T}_m)$ .

It is easy to verify that in the close vicinity of the mean-field critical point the expressions for  $\bar{A}_s^m$  and  $\bar{G}_s^m$  in lowest approximation can be presented in the form,

$$\bar{A}_s^m = u_2 \Delta\bar{T}_m \Delta\bar{v}_m^2 + u_4 \Delta\bar{v}_m^4, \quad \bar{G}_s^m = \bar{A}_s^m - \Delta\bar{v}_m \Delta\bar{P}_m, \quad (12)$$

where  $\Delta\bar{T}_m = \bar{T}_m - \bar{T}_0$ , while  $u_2 = -\frac{1}{2!} \left( \frac{\partial^2 \bar{P}_m}{\partial \bar{T}_m \partial \bar{v}_m} \right)^0$  and  $u_4 = -\frac{1}{4!} \left( \frac{\partial^3 \bar{P}_m}{\partial \bar{v}_m^3} \right)^0$  are the expansion coefficients. The superscript "0" means that the derivative is calculated at the mean-field critical point. Despite the evident similarity of the expansions (Eq. (12)) and the corresponding Landau expansion, Eq. (3), the variable  $\Delta\bar{v}_m$  cannot be identified with the order parameter. Actually in the Landau theory the singular part of the free-energy density is invariant with respect to the replacement  $\varphi_{1m}$  by  $-\varphi_{1m}$ . At the same time, there is no invariance of the free-energy density with respect to the replacement  $\Delta\bar{v}_m$  by  $-\Delta\bar{v}_m$ , except asymptotically close to the critical point.

#### 4. CONNECTION BETWEEN SCALING AND THERMODYNAMIC VARIABLES

In the present work the connection of scaling and thermodynamic quantities in the mean-field approximation are determined as

$$\Delta \bar{P}_m = h_{1m} = \left( \frac{\partial F_m}{\partial \varphi_{1m}} \right)_{h_{2m}}, \quad \bar{G}_s^m = \Phi_m = F_m - \varphi_{1m} \left( \frac{\partial F_m}{\partial \varphi_{1m}} \right)_{h_{2m}}. \quad (13)$$

The above-mentioned quantities are the functions of scaling and thermodynamic variables respectively. Thus, the relations, Eq. (13), are a closed system of these equations. Taking into account the expression, Eq. (3), for  $F_m$ , the connection between the scaling and experimental variables can be obtained as a solution of Eqs. (13). In particular, along the coexistence curve (at the condition  $h_{1m} = 0$ ) one finds

$$\varphi_{1m}^2 = \sqrt{-\frac{\bar{G}_s^m}{u_4}}, \quad h_{2m} = -\frac{2u_4}{u_2} \sqrt{-\frac{\bar{G}_s^m}{u_4}}. \quad (14)$$

Also, by using Eqs. (2) and (11), one can easily obtain the differentials of the scaling fields  $h_{1m}$  and  $h_{2m}$ ;

$$\begin{aligned} dh_{1m} &= d\Delta \bar{P}_m = -\left( \frac{d\bar{P}_s^m}{dT_m} \right) d\bar{T}_m + d\bar{P}_m, \\ dh_{2m} &= -\frac{1}{\varphi_{2m}} [d\bar{G}_s^m + \varphi_{1m} d\Delta \bar{P}_m] \\ &= \frac{1}{\varphi_{2m}} \left( \Delta \bar{v}_m + \varphi_{1m} \left( \frac{d\bar{P}_s^m}{dT_m} \right) \right) d\bar{T}_m + \frac{1}{\varphi_{2m}} (\Delta \bar{v}_m - \varphi_{1m}) d\bar{P}_m. \end{aligned} \quad (15)$$

Note that Eq. (13) and the functional dependences in Eq. (3) for potentials  $\Phi_m$  and  $F_m$  are supposed to be correct in the entire region of the fluid state. Correspondingly, Eq. (13) also give relations between the scaling and experimental variables in the entire region of the fluid state.

#### 5. EFFECTS OF FLUCTUATIONS

Formulation of the thermodynamic potentials and of the connection between scaling and physical measurable variables enables us to take into account the influence of fluctuations in the critical region. In accordance with the theory of critical phenomena, the effects of fluctuations are incorporated by a renormalization group method [8]. Using Eqs. (1) and (2), let us consider the scaling thermodynamic potential  $\Phi$  depending on the scaling field  $h_2$  and the order parameter  $\varphi_1$ . In this case the order parameter

$\varphi_1$  should be considered as a function of the scaling fields  $h_1$  and  $h_2$ . As in the critical region the order parameter  $\varphi_1$  is a strongly fluctuating value, and the scaling potential  $\Phi$  may be represented through the effective Hamiltonian [7,8],

$$\Phi = \frac{1}{\Omega} \ln \left[ \int \exp(-\Omega H_{\text{eff}}) \mathcal{D}\varphi_1 \right]. \quad (16)$$

Here  $\Omega$  is a normalization factor, while the effective Hamiltonian  $H_{\text{eff}}$  with the given order parameter configuration  $\varphi_1(\vec{r})$  can be written in the form,

$$H_{\text{eff}}[\varphi_1] = \frac{1}{V} \int \left[ u_2 h_2 \varphi_1^2(\vec{r}) + u_4 \varphi_1^4(\vec{r}) + c_0 (\nabla \varphi_1(\vec{r}))^2 - h_1 \varphi_1(\vec{r}) \right] d\vec{r}, \quad (17)$$

where  $V$  is the volume of the system and  $c_0$  is a non-universal coefficient,  $c_0 > 0$ . Note that in the absence of fluctuations the order parameter  $\varphi_1$  is equal to its average value  $\varphi_{1m}$ , while the thermodynamic potential  $\Phi$  explicitly reduces to its mean-field limit  $\Phi_m$ . Crossover expressions for the scaling quantities can be calculated as a result of a smoothing procedure within the renormalization group method and  $\varepsilon$ -expansion [9–12]. The crossover expressions obtained after some phenomenological generalization are given in the Appendix. Asymptotically close to the critical point the crossover reproduces the “linear” model of the equation of state [13], whereas far away from the critical point it reduces to the mean-field approximation.

Inclusion of fluctuations in the framework of the phase-transition theory is valid for the scaling quantities. To formulate the crossover equation of state in terms of measurable physical variables, it is necessary to define a relation between the scaling and thermodynamic quantities in the fluctuation region as well as a relation between the crossover quantities and the corresponding mean-field quantities. It is assumed within the suggested approach that the critical parts of the thermodynamic potentials  $\bar{A}$  and  $\bar{G}$  are defined similarly in the mean-field approximation. Moreover, it is supposed that Eq. (13) for the connection between the singular part of the thermodynamic potential and the scaling potential is valid in the fluctuation region as well;

$$\bar{G}_s = \Phi. \quad (18)$$

At the same time, a relation between the thermodynamic field  $\Delta \bar{P}$  and the scaling ordering field  $h_1$  changes and will be determined below. One should also keep in mind that in the crossover procedure experimental values of the critical parameters are used instead of mean-field ones.

## 6. CONNECTION BETWEEN MEAN-FIELD AND CROSSOVER VARIABLES

In the present work it is supposed that the effects of the order-parameter fluctuations do not result in a modification of the scaling fields:

$$h_1 = h_{1m}, \quad h_2 = h_{2m}. \quad (19)$$

Equation (19) determines the relations between the crossover and mean-field scaling variables. In order to obtain the equation of state, it is also necessary to define a relation between the crossover and mean-field thermodynamic variables. Let us assume that the actual measurable dimensionless temperature  $\bar{T}$  and the mean-field dimensionless temperature  $\bar{T}_m$  are equal;

$$\bar{T} = \bar{T}_m. \quad (20)$$

To define a relation between the mean-field and crossover pressure, one should note that in accordance with the theory of critical phenomena the coexisting curve of one-component fluids is determined by the condition  $h_1 = 0$ . It means that the scaling ordering field  $h_1$  is proportional to the dimensionless deviation of the real pressure  $\bar{P}$  from the saturation pressure  $\bar{P}_s(\bar{T})$ :

$$h_1 = \omega_p \Delta \bar{P}, \quad (21)$$

where  $\Delta \bar{P} = \bar{P} - \bar{P}_s(\bar{T})$  and  $\omega_p$  is a coefficient. Hence, taking into account Eqs. (13) and (19) one obtains  $\Delta \bar{P}_m = \omega_p \Delta \bar{P}$ . A natural requirement of simultaneous vanishing of the values  $\bar{P}$  and  $\bar{P}_m$  results in the relation,

$$\bar{P}_m = \omega_p \bar{P}. \quad (22)$$

The scaling factor  $\omega_p = \bar{P}_s^m / \bar{P}_s$  depends on the dimensionless temperature  $\bar{T}$ .

The crossover expressions for other thermodynamic quantities can be obtained by differentiation of corresponding potentials. In particular, using the differential relation, Eq. (11), for the quantity  $\bar{G}_s$ , as well as Eqs. (2) and (18)–(21), one can find

$$\begin{aligned} \Delta \bar{v} &= - \left( \frac{\partial \bar{G}_s}{\partial \bar{P}} \right)_{\bar{T}} = - \left( \frac{\partial \Phi}{\partial \bar{P}} \right)_{\bar{T}} = \varphi_2 \left( \frac{\partial h_2}{\partial \bar{P}} \right)_{\bar{T}} + \varphi_1 \left( \frac{\partial h_1}{\partial \bar{P}} \right)_{\bar{T}} \\ &= \omega_p \left( \varphi_1 + \varphi_2 \left( \frac{\partial h_{2m}}{\partial \bar{P}_m} \right)_{\bar{T}_m} \right). \end{aligned}$$



Taking into account the differential relations, Eq. (15), one can obtain

$$\Delta\bar{v} = \omega_p \left( \varphi_1 + \frac{\varphi_2}{\varphi_{2m}} [\Delta\bar{v}_m - \varphi_{1m}] \right). \quad (23)$$

Indeed, Eqs. (20), (22), and (23) determine a new crossover equation of state for one-component fluids and can be used for the description of experimental data.

## 7. INITIAL EQUATION OF STATE

To illustrate possibilities of the suggested approach for the description of one-component fluid thermodynamic properties, the following four-parametric cubic equation is used as an initial mean-field equation of state:

$$\bar{P}_m = \frac{\bar{T}}{(\bar{a}_1 - \Delta\bar{v}_m)} - \frac{\bar{a}_2\omega}{(\bar{a}_3 - \Delta\bar{v}_m)} + \frac{\bar{a}_2\omega}{(\bar{a}_4 - \Delta\bar{v}_m)}, \quad (24)$$

where

$$\omega = 1 + m_1 \left( 1 - \sqrt{\bar{T}} \right) + m_2 \left( 1 - \sqrt{\bar{T}} \right)^2. \quad (25)$$

In the chosen way of normalization of the thermodynamic variables, the coefficients  $\bar{a}_2$ ,  $\bar{a}_3$ , and  $\bar{a}_4$  are expressed through the coefficient  $\bar{a}_1$ :

$$\begin{aligned} \bar{a}_2 &= -\frac{(1 - \bar{a}_1)^2}{\sqrt{1 - 4\bar{a}_1}}, & \bar{a}_3 &= \frac{1}{2} (1 - \bar{a}_1) \left[ 1 + \sqrt{1 - 4\bar{a}_1} \right], \\ \bar{a}_4 &= \frac{1}{2} (1 - \bar{a}_1) \left[ 1 - \sqrt{1 - 4\bar{a}_1} \right]. \end{aligned} \quad (26)$$

To complete the model it is necessary to define the function  $\omega_p$  (see Eqs. (22) and (23)). This function is written similarly to Eq. (25);

$$\omega_p = 1 + k_1 \left( 1 - \sqrt{\bar{T}} \right) + k_2 \left( 1 - \sqrt{\bar{T}} \right)^2. \quad (27)$$

Thus, the universal crossover model is formulated entirely. Equations (20) and (22)–(27) enable us to calculate the thermodynamic properties of one-component fluids in a wide range of the thermodynamic variables including the critical region. In particular, to calculate  $P$ – $\rho$ – $T$  dependencies, the presented crossover model contains ten non-universal parameters:  $T_c$ ,  $P_c$ ,  $\rho_c$ ,  $\bar{a}_1$ ,  $m_1$ ,  $m_2$ ,  $k_1$ ,  $k_2$ ,  $Gi$ , and  $g$  (see Appendix). These parameters are individual for each substance and can be found from the best correlation between the calculations and experiment.

## 8. COMPARISON WITH EXPERIMENT

Various algorithms can be used to calculate the thermophysical properties of fluids with the proposed crossover model. For instance, the calculation of isothermal properties of fluids in the one-phase region reduces to the calculation of density  $\rho$  at the given experimental values of temperature  $T$  and pressure  $P$ . Having a set of initial values of the non-universal parameters and using conditions in Eqs. (20) and (22), one can find the values of  $\Delta\bar{v}_m$  as well as  $\varphi_{1m}$ ,  $\varphi_{2m}$ ,  $h_{1m}$ , and  $h_{2m}$  in the mean-field approximation. Then, using the conditions in Eq. (19) and the expressions in Eq. (A1) one can find the respective values of the parametric variables  $r$  and  $\theta$  in order to calculate the scaling densities  $\varphi_1$  and  $\varphi_2$ . Finally, by substituting all essential values into the expression, Eq. (23), it is possible to find the fluid density  $\rho$ .

The values of the crossover adjustable parameters are found within the optimization procedure under the condition of the best correlation between the calculated and experimental data. In this work the crossover equations of state are obtained for methane, ethane, carbon dioxide, and water. The standard simulated reference data [14] are used as the initial data for optimization of the non-universal parameters. These reference data demonstrate good agreement with accurate experimental data.

For optimization of the crossover-model parameters, the experimental saturation pressure  $P(T)$  and liquid–vapor coexisting curve  $\rho(T)$  are used. The calculation algorithm for the phase equilibrium fluid properties is the same as that for calculation of isothermal properties. The only difference is the condition for the scaling and mean-field ordering fields to be zero:  $h_1 = h_{1m} = 0$ . The calculations are made at the given experimental value of temperature  $T$ . The system-dependent parameters were determined by the best description requirement of the standard simulated data. The values of the parameters are listed in Table I. It should be noted that within the optimization procedure the values of the critical parameters  $T_c$  and  $P_c$  were fixed on the values recommended by the standard data [14]. The critical densities  $\rho_c$  were considered as adjustable parameters. As one can see Table I, the obtained values of the critical densities are slightly smaller than the recommended values.

The calculated  $P(T)$  and  $\rho(T)$  dependences in comparison with the simulated data of the liquid–vapor equilibrium for methane, ethane, carbon dioxide, and water are presented in Figs. 1–4. As can be seen in the figures, the proposed crossover approach provides a good correlation between the crossover model and the simulated data along the coexistence curves in the entire region of the fluid existence excluding the immediate vicinity of the critical point (see insets in Figs. 1–4). The deviations of the

**Table I.** Non-universal Parameters of the One-Component Fluid Crossover Equations of State

	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO <sub>2</sub>	H <sub>2</sub> O
$\bar{a}_1$	0.1704	0.1726	0.1694	0.1505
$m_1$	-0.1350	0.0731	0.2272	0.2930
$m_2$	1.1194	1.3374	1.8689	1.8823
$k_1$	0.6501	0.6014	0.6665	0.6534
$k_2$	-0.5816	-0.4938	0.1111	-0.9813
$Gi$	0.1396	0.1357	0.1273	0.1007
$g$	0.0860	0.1130	0.0955	0.2337
$T_c$ (K)	190.564	305.33	304.1282	647.096
$P_c$ (MPa)	4.5992	4.8718	7.3773	22.064
$\rho_c$ (mol·dm <sup>-3</sup> )	9.8553 <sup>a</sup>	6.6060 <sup>a</sup>	10.1938 <sup>a</sup>	17.1563 <sup>a</sup>
	10.139 <sup>b</sup>	6.8897 <sup>b</sup>	10.6249 <sup>b</sup>	17.8737 <sup>b</sup>
$z_c$	0.2946	0.2905	0.2862	0.2390

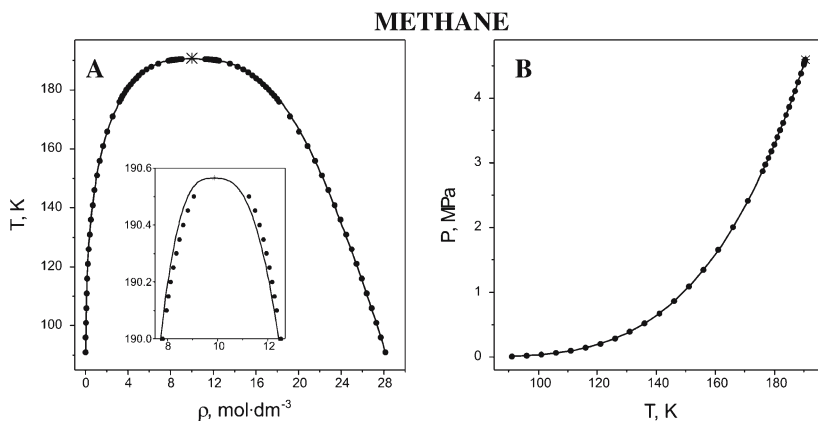
<sup>a</sup>Optimized values of the critical densities.

<sup>b</sup>Recommended values of the critical densities [14].

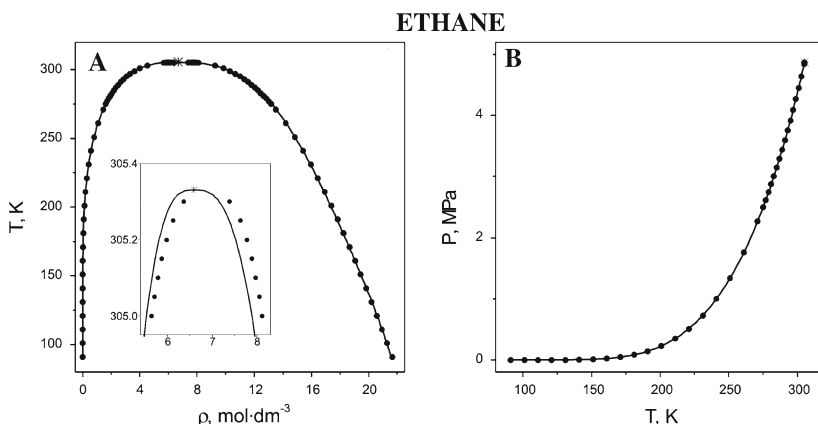
calculated densities from the simulated data in the critical region could be associated with a shift of the critical density  $\rho_c$ . Our attempts to fix  $\rho_c$  on the values recommended by the standard data simulator resulted in some improvement in the correlation close to the critical point, but the quality of the description in the remaining region was considerably deteriorated. This feature is typical for each substance for which the optimization of the crossover model is performed.

Besides the phase equilibria, the calculations of isothermal properties in comparison with the simulated data are presented in Figs. 5–8. Since the one-phase isothermal data were not used for the optimization of the crossover model, the presented results illustrate the predictive capabilities of the crossover equation of state. As one can see in the figures, calculations for near-critical isotherms correlate with the standard simulated data worse than for high- and low-temperature isotherms. It should be noted also that inclusion of the simulated isothermal data into the optimization procedure does not lead to significant improvements in the description of the one-phase region.

Thus, in the framework of the proposed crossover model it is possible to obtain the global equations of state for real one-component fluids, which allow calculation of thermophysical properties in the one- and two-phase regions. The calculation results are in good agreement with the experimental data in the entire region of the fluid state with the exception of the immediate vicinity of the critical point. Essential discrepancies and apparent shifts of the critical density values in the crossover



**Fig. 1.** Coexistence curve (A) and saturation-pressure curve (B) for methane. Lines correspond to the crossover-model optimization. The star indicates the location of the critical point for the crossover equation of state. The symbols “•” represent the standard simulated data [14]. Inset shows the immediate vicinity of the critical point.



**Fig. 2.** Coexistence curve (A) and saturation-pressure curve (B) for ethane. Notations are the same as in Fig. 1.

equations of state are obvious defects of the proposed model. They can be caused by different reasons. First, a descriptive ability of the crossover model is evidently connected to the transition from the fluctuation behavior of thermodynamic properties in the near-critical region to the mean-field behavior far from the critical point. In the present work this transition is provided by the crossover function  $\mathcal{Y}$  (see Appendix). The expression, Eq. (A3), for the crossover function corresponds to some phenomenological generalization for the one-loop approximation of the

CARBON DIOXIDE

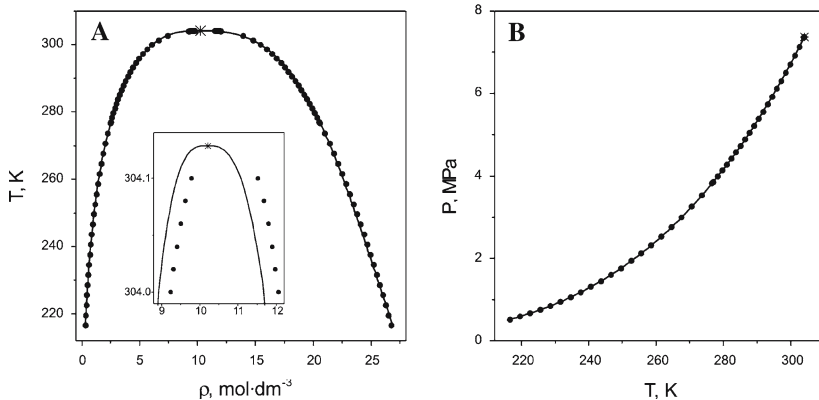


Fig. 3. Coexistence curve (A) and saturation-pressure curve (B) for carbon dioxide. Notations are the same as in Fig. 1.

WATER

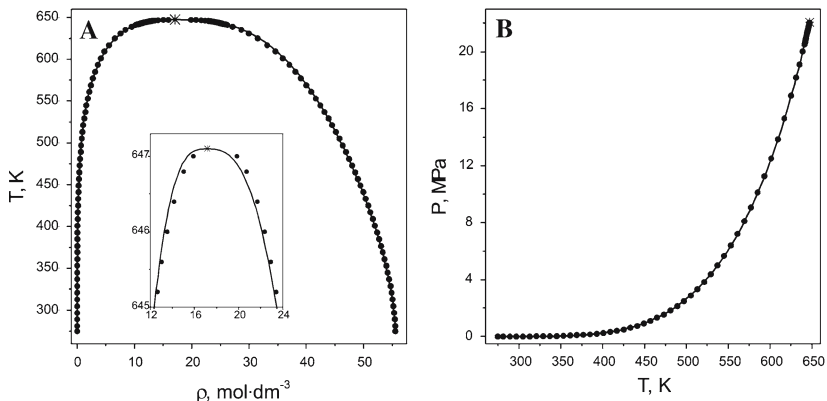
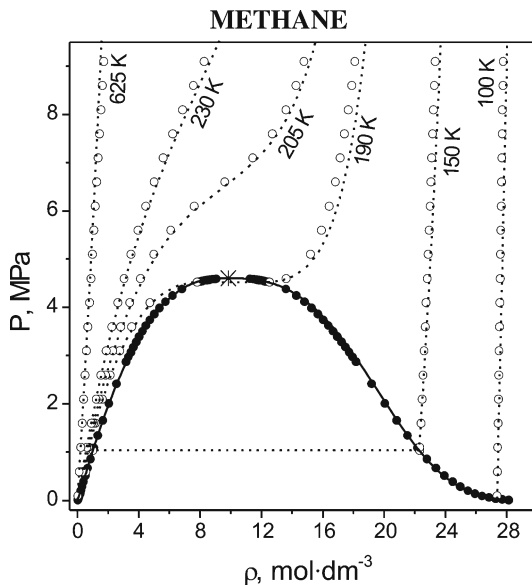


Fig. 4. Coexistence curve (A) and saturation-pressure curve (B) for water. Notations are the same as in Fig. 1.

renormalization-group method. Being an approximation the expression, Eq. (A3), is imperfect. Secondly, the accuracy of the experimental-data description within the crossover model depends essentially on the initial mean-field equation of state. In particular, the use of a two-parametric cubic equation [2] as the initial mean-field equation of state makes agreement with experiment considerably worse.

However, the most important reason for the defects mentioned above is a fundamental problem associated with the singular diameter of the



**Fig. 5.** Phase equilibria and isotherms of methane. Lines correspond to the crossover equation of state. Solid line represents the coexistence curve. Dashed lines are predictions for the isotherms. The star marks the critical point for the crossover equation of state. Symbols represent the standard simulated data [14]: the solid circles “•” show the coexistence curve and the open circles “o” are the isothermal data.

liquid–vapor coexistence curve. The presented crossover model gives the following result for the singular diameter close to the critical point:

$$d_s = \frac{1}{2} [(\rho_l - \rho_c) + (\rho_g - \rho_c)] \cong B_1 |\tau|^{2\beta} + B_2 |\tau|^{1-\alpha}, \quad (28)$$

where  $\tau = T/T_c - 1$  and the coefficients  $B_1$  and  $B_2$  are non-universal constants. This dependence agrees with the corresponding expression within the “complete scaling” model [15, 16]. The presence of the term  $\propto |\tau|^{2\beta}$  in the expression, Eq. (28), is associated with a particular selection of the ordering field and the thermodynamic potential. However, in our model the coefficients  $B_1$  and  $B_2$  are not independent as the ordering field is associated with pressure and temperature only and does not include a contribution from the chemical potential. This constraint can lead to a critical density shift and, as a result, to some distortion in the description of the critical region.

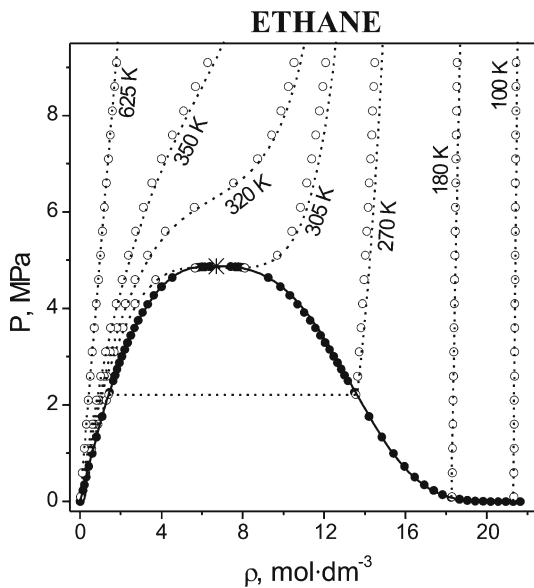


Fig. 6. Phase equilibria and isotherms of ethane. Notations are the same as in Fig. 5.

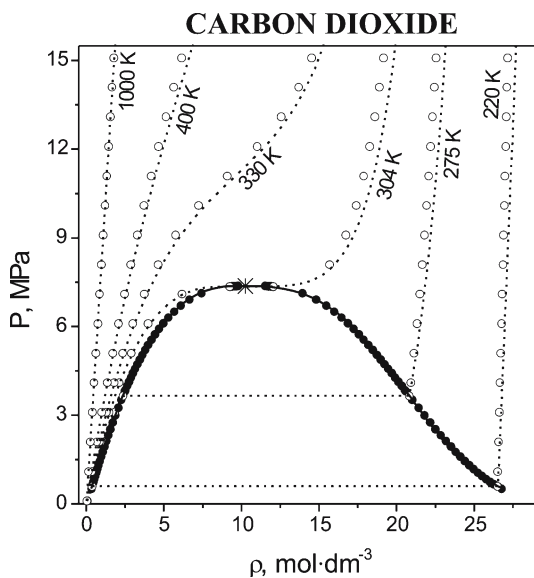


Fig. 7. Phase equilibria and isotherms of carbon dioxide. Notations are the same as in Fig. 5.

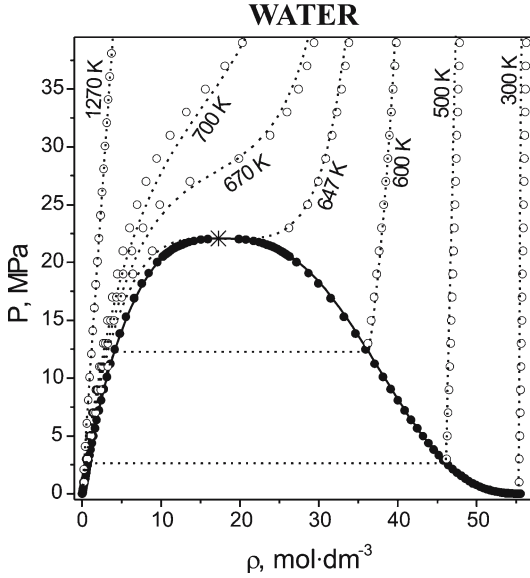


Fig. 8. Phase equilibria and isotherms of water. Notations are the same as in Fig. 5.

In this respect, we anticipate that the choice of the ordering field as a linear combination of pressure, temperature, and chemical potential, as proposed by the “complete scaling”, can provide a more adequate description of the standard simulated data in the critical region.

**APPENDIX**

Phenomenological generalized crossover expressions for the scaling thermodynamic quantities are conveniently presented in the parametric form. In this case,

$$\begin{aligned}
 h_2 &= r \mathcal{Y}^{\frac{\gamma-1}{\Delta}} \left( 1 - \frac{\lambda_1}{s^2} \theta^2 \right), \\
 h_1 &= \frac{b_1 s}{\lambda_2} \sqrt{\frac{u_2^3}{u_4}} G i^{\frac{1}{2}(1+\alpha-\gamma)} r^{\gamma+\beta} \mathcal{Y}^{\frac{(\gamma-2\beta)}{2\Delta}} \frac{\mathcal{Z}_h}{\vartheta_s^2} \theta \left[ \vartheta_s^2 - \theta^2 \right], \\
 \varphi_1 &= \sqrt{\frac{u_2}{u_4 s^2}} G i^{\frac{1}{2}-\beta} r^\beta \mathcal{Y}^{\frac{(\gamma-2\beta)}{2\Delta}} \theta, \\
 \varphi_2 &= \frac{(2-\alpha)}{\lambda_2} \frac{u_2^2}{u_4} G i^\alpha r^{1-\alpha} \mathcal{Y}^{\frac{(1-2\beta)}{\Delta}} \frac{\mathcal{Z}_{as}}{\vartheta_{as}^2} \left[ \vartheta_{as}^2 - \theta^2 \right] - \frac{2}{\lambda_2} \frac{u_2^2}{u_4} h_2.
 \end{aligned}
 \tag{A1}$$



Here the variable  $r$  has a meaning of the generalized distance to the critical point, and the value  $\theta$  sets a deviation from the critical isochore. The values of the critical indexes  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\Delta$  in the expressions, Eq. (A1), correspond to the universality class of the three-dimensional Ising model [17, 18]:

$$\alpha = 0.110, \quad \beta = 0.3255, \quad \gamma = 1.239, \quad \Delta \cong 0.5. \tag{A2}$$

In this work for the crossover function  $\mathcal{Y}$  the two-parametric generalized form is used;

$$\mathcal{Y} = 1 + q - \frac{q}{\left(g + q^{\frac{\gamma}{\Delta}}\right)^{\frac{\Delta}{\gamma}}}, \tag{A3}$$

where  $q = (r/Gi)^\Delta$ ,  $Gi$  is the Ginzburg parameter, and  $g$  is an additional non-universal parameter which characterizes the transformation to the mean-field limit ( $q \cong g$ ). The amplitude crossover functions  $\vartheta_s$ ,  $\vartheta_{as}$ ,  $\mathcal{Z}_{as}$ , and  $\mathcal{Z}_h$  have a form:

$$\begin{aligned} \vartheta_s^2 &= \frac{(1 + e_1 \bar{q})}{\left[1 + \frac{\beta}{\gamma} \{D - 1\} + \frac{\beta}{\gamma} e_2 \{D + 1\} \bar{q}\right]}, \\ \vartheta_{as}^2 &= \frac{\gamma(\gamma - 1)}{(1 - \alpha)(\gamma - 2\beta)} \frac{(1 + \bar{e}_1 \bar{q})}{\left[1 + \frac{(\gamma - \alpha)}{2(1 - \alpha)} \{\bar{D} + 1\} \bar{q}\right]}, \\ \mathcal{Z}_{as} &= \frac{\left[1 + \bar{e}_1 \left(1 - \frac{b_2}{4} \{1 - \bar{D}\} \theta^2\right) \bar{q} \hat{G}\right]}{\left[1 + \gamma \bar{q} \hat{G}\right]}, \\ \mathcal{Z}_h &= \frac{\left[1 + e_1 \bar{q} \hat{G} + \frac{\beta}{\gamma} (1 + e_2 \bar{q}) \{D - 1\} \theta^2 \hat{G}\right]}{\left[1 + \gamma \bar{q} \hat{G}\right]}, \end{aligned} \tag{A4}$$

where

$$\begin{aligned} D &= \sqrt{1 + \frac{e_3 \bar{q}}{(1 + e_2 \bar{q})^2}}, & \bar{D} &= \sqrt{1 - \frac{\bar{e}_3 \bar{q}}{(1 + \bar{e}_2 \bar{q})^2}}, \\ \hat{G} &= \frac{1}{\left[1 - \left(1 - \frac{2\beta}{\gamma}\right) \theta^2\right]}. \end{aligned} \tag{A5}$$

Argument  $\bar{q}$  in Eqs. (A4) and (A5) is defined as

$$\bar{q} = \frac{x}{(1 - x)}, \quad x = \frac{q}{\mathcal{Y}} \frac{d\mathcal{Y}}{dq}. \tag{A6}$$

The universal constants  $s^2$ ,  $\lambda_i$ ,  $b_i$ ,  $e_i$ , and  $\bar{e}_i$  in Eqs. (A1), (A4), and (A5) can be expressed through the critical exponents:

$$\begin{aligned}
 s^2 &= \frac{\gamma(1-2\beta)(1+\gamma-\alpha)}{2\beta(1-\alpha)(\gamma-1)}, \\
 \lambda_1 &= \frac{(\gamma-2\beta)(1+\gamma-\alpha)}{2\beta(1-\alpha)(\gamma-1)}, & \lambda_2 &= \frac{\alpha(\gamma-2\beta)(1+\gamma-\alpha)^2}{\gamma(1-\alpha)(\gamma-1)^2}, \\
 b_1 &= 2\alpha \frac{(2-\alpha)(1-\alpha)(\gamma-2\beta)}{\gamma^2(\gamma-1)(1-2\beta)}, & b_2 &= (2-\alpha) \frac{(\gamma-\alpha)(\gamma-2\beta)}{\gamma^2(\gamma-1)}, \\
 e_1 &= 2\beta\gamma \frac{(1+\gamma-\alpha)^2}{(1-\alpha)(2-\alpha)}, & e_2 &= \gamma \frac{(2\gamma-1)}{(1-\alpha)}, & e_3 &= 4\gamma \frac{(\gamma-1)(\gamma-2\beta)}{(1-\alpha)(2-\alpha)}, \\
 \bar{e}_1 &= \frac{2\gamma}{(2-\alpha)}, & \bar{e}_2 &= \frac{(\gamma-\alpha)}{2\beta}, & \bar{e}_3 &= \frac{2\alpha(\gamma-1)}{\beta(2-\alpha)}.
 \end{aligned}
 \tag{A7}$$

In the immediate vicinity to the critical point

$$\begin{aligned}
 q &\rightarrow 0, & \bar{q} &\rightarrow 0, & \mathcal{Y} &\rightarrow 1, & \vartheta_s &\rightarrow 1, \\
 \vartheta_{\text{as}} &\rightarrow \frac{\gamma(\gamma-1)}{(1-\alpha)(\gamma-2\beta)}, & Z_{\text{as}} &= Z_h \rightarrow 1,
 \end{aligned}$$

and the expressions in Eq. (A1) reduce to the original definitions for the scaling variables in the “linear” model [13].

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