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A Scaled Equation of State for Real Fluids in the Critical Region

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A scaled equation of state is proposed for real fluids in the critical region which incorporates asymmetry with respect to the critical isochore. In the range of reduced densities $0.65 \leqslant (\rho/\rho_c) \leqslant 1.4$ and for reduced temperatures $(T/T_c) \leqslant 1.2$, the equation represents P–V–T data for steam within the experimental accuracy.

KEY WORDS: critical phenomena; equation of state; scaling laws; steam; thermodynamic properties.

1. INTRODUCTION

Recently, extended scaling theory (ST) has been used successfully for calculations of the thermophysical properties of fluids in a broad vicinity of the critical point. Its success is due to the fact that scaling theory has a microscopic justification [1, 2]. Furthermore, the addition of non-asymptotic correction terms in the scaled equation of state made it possible to increase considerably the precision and the range of approximation [3–5]. The ST equations used for those calculations have been obtained for the symmetric lattice-gas model. In such a system, the chemical potential along the critical isotherm is an odd function of $\Delta\rho = (\rho - \rho_c)/\rho_c$, the dimensionless density deviation from the critical value ρ_c. The singular part of the free energy and isochoric heat capacity and the isothermic compressibility are even functions of $\Delta\rho$. The densities at the coexistence curve diameter $\rho_d = (\rho_L + \rho_G)/2$ do not depend on temperature and coincide with the critical isochore $\rho \equiv \rho_c$. Thus in the lattice-gas model the critical isochore $\rho = \rho_c$ is a line of symmetry for the thermodynamic properties. In

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a real fluid the situation is quite different. Calculations show that the precision of the description and the width of the approximation region in pure liquids [5–6], and in binary mixtures [7] are greatly influenced by the asymmetry with respect to the critical isochore. It is therefore of great importance to investigate the influence of this asymmetry on the properties of fluids in the critical region.

A constructive approach to the solution of this problem was proposed by Pokrovsky [8], who showed that fluctuations of particles of density Δn and energy ΔE at a constant volume $V = V_c$ for a liquid are not statistically independent $(\langle \Delta n\, \Delta E\rangle_{V=V_c} \neq 0)$. This means that in accordance with fluctuation theory [9], Δn and ΔE can be represented as linear combinations of the corresponding quantities for the symmetric system. As a consequence of such a transformation of the variables Δn and ΔE, it appears [8, 10] that the coexistence curve diameter has a singular behavior $\rho_d \sim |\tau|^{1-\alpha}$, where $\tau = (T - T_c)/T_c$ is the dimensionless deviation of the temperature T from the critical value T_c.

In this paper an equation of state for real fluids in the critical region with allowance for asymmetry with respect to the critical isochore is obtained on the basis of the Pokrovsky transformations and the extended scaling theory.

2. THE POKROVSKY TRANSFORMATIONS

Following the Pokrovsky transformations, let us represent fluctuations of the number of particles ΔN and those of the entropy $\Delta S = S - S_c$, which differ from the energy density only by the factor $T_c^{-1}[\Delta S = (-T_c^{-1})\,\Delta E]$, in the form of the linear combinations of the corresponding symmetric quantities

$$\Delta N = \Delta N_{LG} + v\Delta S_{LG} \tag{1a}$$

$$\Delta S = u\Delta N_{LG} + \Delta S_{LG} \tag{1b}$$

The "fields" $\Delta\mu$ and τ conjugate to the quantities ΔN and ΔS are related to the thermodynamic potential Ω by

$$N = -\frac{\rho_c}{P_c}(\partial\Omega/\partial\mu)_\tau, \qquad S = -\frac{1}{T_c}(\partial\Omega/\partial\tau)_{\Delta\mu} \tag{2}$$

They are also linear combinations of the quantities $\Delta\mu_{LG}$ and τ_{LG}

$$\Delta\mu = u_1\, \Delta\mu_{LG} + u_2\tau_{LG} \tag{3a}$$

$$\tau = v_1\, \Delta\mu_{LG} + v_2\tau_{LG} \tag{3b}$$

where $\Delta\mu = (\rho_c/P_c)[\mu(\rho, \mathrm{T}) - \mu_0(\mathrm{T})]$ is a dimensionless chemical potential, P_c is the critical pressure, and u_1, u_2, v_1, and v_2 are new constants of the transformation. The connection between the constants u and v in Eqs. (1a) and (1b), on one hand, and the constants u_1, u_2, v_1, and v_2, on the other, may be derived from the condition

$$\Delta\mu\Delta N + \Delta S\tau \equiv \Delta\mu_{\mathrm{LG}}\,\Delta N_{\mathrm{LG}} + \Delta S_{\mathrm{LG}}\tau_{\mathrm{LG}} \tag{4}$$

The condition as given by Eq. (4) means that the effective Hamiltonian of a real "asymmetric" system corresponds in first approximation to that of the lattice-gas symmetric model. Asymmetry manifests itself by the appearance of the terms $\sim\Delta N^2\Delta\mu$ in the effective Hamiltonian, which disturb its symmetry with respect to transformations $\Delta\mu \rightarrow -\Delta\mu$ and $\Delta N \rightarrow -\Delta N$ [11]. The Pokrovsky transformations in the form given by Eqs. (1) and (3) do make it possible to take into account the appearance of these terms in the efective Hamiltonian on the phenomenological level by mixing the variables ΔN and ΔS with the quantities $\Delta\mu$ and τ. The condition given by Eq. (4) gives the rule of such a mixing, which in view of Eqs. (1) and (3), can be rewritten in the form

$$\Delta\mu = \frac{1}{1-uv}\Delta\mu_{\mathrm{LG}} - \frac{u}{1-uv}\tau_{\mathrm{LC}} \tag{5a}$$

$$\tau = \frac{1}{1-uv}\tau_{\mathrm{LG}} - \frac{v}{1-uv}\Delta\mu_{\mathrm{LG}} \tag{5b}$$

3. APPLICATION TO CALCULATIONS OF THERMODYNAMIC PROPERTIES

As an equation of state for the lattice-gas symmetric model, we have used the Schofield parametric representation [12], which has a theoretical justification [13]. With allowance for the nonasymptotic terms, obtained by the ε-expansion method [14], the equation of state is determined by the elimination of the variables Γ and θ from the following system of correlations:

$$\Delta\mu_{\mathrm{LG}} = a\Gamma^{\beta\delta}\theta(1-\theta^2) + c\Gamma^{\beta\delta+\Delta}\theta \tag{6}$$

$$\tau_{\mathrm{LG}} = \Gamma(1-b^2\theta^2) \tag{7}$$

$$\Delta\rho_{\mathrm{LG}} = \kappa\Gamma^{\beta}\theta \tag{8}$$

The singular part of the free energy for the lattice gas, $\psi_{\mathrm{LG}}(\Gamma, \theta) = \int \Delta\mu d(\Delta\rho)$, then has the form

$$\psi_{\mathrm{LG}}(\Gamma,\theta)=\frac{ak}{2b^4}\Gamma^{2-\alpha}\left[\frac{2\beta(b^2-1)}{2-\alpha}+\frac{2\beta(2\gamma-1)}{\gamma(1-\alpha)}(1-b^2\theta^2)+\frac{(2\beta-1)}{\alpha}(1-b^2\theta^2)\right]-\frac{kc}{2b^2}\frac{\Gamma^{2-\alpha+\Delta}}{1-\alpha+\Delta}\left[(1-2\beta)b^2\theta^2-\frac{\gamma+\Delta}{2-\alpha+\Delta}\right] \tag{9}$$

Here a, c, and k are constants connected with the individual properties of the substance, and α, β, δ, and γ are the critical exponents for the isochoric heat capacity, the coexistence curve, the critical isotherm, and the isothermal compressibility, respectively. According to the scaling theory these exponents are universal quantities; the exponent Δ in the nonasymptotic term is also universal. Finally, $b^2=(\gamma-2\beta)/\gamma(1-2\beta)$ and $k=[(b^2-1)/|Z_0|]^\beta$, where Z_0 is the value of the parameter $Z=\tau/|\Delta\rho|^{1/\beta}$ on the coexistence curve.

Equations (7) and (8) enable us to perform the transition in the plane of the curvilinear coordinates $\Gamma-\theta$ to the variables $T-\rho$ in the case of the symmetric model. Equations relating the parameters Γ and θ to the dimensionless temperature τ and density $\Delta\rho$ of the real asymmetric system are

$$\tau=\frac{1}{1-uv}\Gamma(1-b^2\theta^2)-\frac{v}{1-uv}\left[a\Gamma^{\beta\delta}\theta(1-\theta^2)+c\Gamma^{\beta\delta+\Delta}\theta\right] \tag{10}$$

$$\Delta\rho=k\Gamma^\beta\theta+v\left\{\frac{a\kappa\gamma(\gamma-1)}{2b^2\alpha(1-\alpha)}\Gamma^{1-\alpha}\left[1-\frac{(1-2\beta)(1-\alpha)}{\gamma-1}b^2\theta^2\right]-\frac{kc(\gamma+\Delta)}{2b^2(1-\alpha+\Delta)}\Gamma^{1-\alpha+\Delta}\right\} \tag{11}$$

The parameter v turns out to be related to the amplitude of the singular part of the coexistence-curve diameter in accordance with the expansion of $\Delta\rho$ at the coexistence curve:

$$\Delta\rho=\pm B_0|\tau|^\beta\pm B_1|\tau|^{\beta+\Delta}+B_2(-\tau)^{1-\alpha}+B_3(-\tau) \tag{12}$$

Substituting into Eqs. (10) and (11) $\theta=\pm1$, which values in the $c=0$ approximation correspond to the coexistence curve, and comparing the terms with the same powers of τ in Eqs. (11) and (12), we obtain

$$v=-B_2\alpha(1-\alpha)b^2(b^2-1)^{1-\alpha}/a\kappa\beta(1-2\beta) \tag{13}$$

Let us analyze on the basis of these expressions the influence of the real liquid asymmetry on the behavior of some thermodynamic quantities in the critical region. In particular, the equations for the isothermal compressibility $K_{\mathrm{T}} = (1/\rho^2)(\partial\rho/\partial\mu)_T$ and the isochoric heat capacity $C_{\mathrm{v}} = T(\partial S/\partial T)_\rho$ can be written in the form

$$K_{\mathrm{T}}^{*} = \frac{P_{\mathrm{c}}}{\rho_{\mathrm{c}}^{2}}\,\rho^2 K_{\mathrm{T}} = \frac{k}{a}\,\Gamma^{-\gamma}\,\frac{1 - 2va\gamma\theta\Gamma^{\gamma+\beta-1} + \mathrm{O}(v^2 r^{\gamma-\alpha})}{1 + (2\gamma b^2 - 3)\theta^2} \tag{14}$$

$$\frac{T_{\mathrm{c}}^{2}\rho c_{\mathrm{v}}}{P_{\mathrm{c}}T} = (1-uv)^2 A\Gamma^{-\alpha}[1 + 2va\gamma\theta\Gamma^{\gamma+\beta-1} + \mathrm{O}(v^2)] - \frac{\rho}{\rho_{\mathrm{c}}}\,M''(T) - \varphi''(\mathrm{T}) \tag{15}$$

where $A = [a\kappa\gamma(\gamma-1)/2b^2\alpha]$ and $M''(\tau)$ and $\varphi''(\tau)$ are analytical functions of temperature.

It is obvious from these equations that the parameter u does not enter into the expression for isothermal compressibility. In the other measurable quantities τ and C_{v}, it enters in the form of combination (uv) in the expression $(1-uv)$, which does not make it possible to derive this quantity from the experimental data. In this sense the parameters u and v in the Pokrovsky transformations given by Eqs. (1a) and (1b) are not equivalent.

The behavior of the curve of maximum isothermal compressibility, K_{T}^{*}, is also of interest. In the symmetric lattice-gas model the K_{T}^{*} maxima coincide with the critical isochore $\rho = \rho_{\mathrm{c}}$ $(\Delta\rho = 0)$. To obtain the equation for the K_{T}^{*} maxima in a real asymmetric system, let us differentiate Eq. (14) with respect to $\Delta\rho$. Then after algebraic transformations in the linear approximation in v and θ from Eqs. (10), (11), and (14), we obtain

$$\theta_{\max} = -\frac{va\gamma}{2(b^2\gamma - 1)}\,\Gamma^{1-\alpha-\beta} \tag{16}$$

It is convenient to rewrite this expression in some other form. By substitution of Eq. (15) in Eq. (11) with account of Eq. (13) and by replacing critical exponents by their numerical values, we obtain

$$\Delta\rho_{\max} \approx B_2\tau^{1-\alpha} \tag{16a}$$

This means that the line of K_{T}^{*} maxima in a one-phase region in first approximation is the reflection of the line of the symmetry (the line of the "singular" diameter) in the two-phase region.

For further analysis of the equations let us consider the behavior of the mentioned properties on some selected lines and compare the obtained correction terms with the next-order approximation of the scaling theory.

Table I. Corrections of the Asymptotic Laws with Account of Transformations Given by Eqs. (1) and (5)

Thermodynamic quantity	Selected line	Asymptotic behavior	Accounting of nonasymptotic term	Accounting of asymmetry
$(T_c^2 \rho C_v / P_c \mathrm{T})$	$\rho = \rho_c$ $T = T_c$	$\tau^{-\alpha}$ $\|\Delta\rho\|^{-\alpha/\beta}$	$\tau^{-\alpha+\Delta}$ $\|\Delta\rho\|^{(-\alpha+\Delta)/\beta}$	$\tau^{-\alpha+(\gamma-\alpha)}$ $\pm\|\Delta\rho\|^{[-\alpha+(\gamma+\beta-1)]/\beta}$
$P_c(\rho^2/\rho_c^2) K_T$	$\rho = \rho_c$ $T = T_c$	$\tau^{-\gamma}$ $\|\Delta\rho\|^{-\gamma/\beta}$	$\tau^{-\gamma+\Delta}$ $\|\Delta\rho\|^{(-\gamma+\Delta)/\beta}$	$\tau^{-\gamma+(\gamma-\alpha)}$ $\pm\|\Delta\rho\|^{[-\gamma+(\gamma+\beta-1)]/\beta}$
$(\rho_L - \rho_G)/2\rho_c$	$T = T_S$	$\|\tau\|^{\beta}$	$\|\tau\|^{\beta+\Delta}$	—
$(\rho_L + \rho_G)/2\rho_c$	$T = T_S$	—	—	$\|\tau\|^{1-\alpha} + \mathrm{O}(\|\tau\| + \|\tau\|^{1-\alpha+\Delta})$
$(\partial^2 \mu / \partial \mathrm{T}^2)_\rho$	$\rho = \rho_c$ $T = T_c$	— $\pm\|\Delta\rho\|^{(-\alpha-\beta)/\beta}$	— $\pm\|\Delta\rho\|^{(-\alpha-\beta+\Delta)/\beta}$	$\tau^{\gamma-1-\alpha}$ $\|\Delta\rho\|^{[-\alpha-\beta+(\gamma+\beta-1)]/\beta}$

Namely, let us consider nonasymptotic corrections on the critical isochore ($\Delta\rho = 0$, $\Gamma \sim |\tau|$, $\theta \sim |\tau|^{1-\alpha-\beta}$) and on the critical isotherm [$\tau = 0$, $\Gamma \sim |\Delta\rho|^{1/\beta}$, $|\theta| \sim 1/b + \mathrm{O}(\Gamma^{\beta\delta-1})$] and compare them with the terms $\sim c\Gamma^{\beta\delta+\Delta}$ in Eqs. (6) and (10). The results of this analysis are presented in Table I. As follows from the Table I, the exponents for the nonasymptotic terms connected with the asymmetry are substantially large than the nonasymptotic terms ($\Delta \approx 0.5$, $\gamma - \alpha \approx 1.1$) on the critical isochore. In addition, since $\gamma - 2\alpha \approx 1$, it is difficult to distinguish between asymmetric corrections for the isochoric heat capacity and the regular terms $\sim\tau$ which appear due to expansion of the functions $M''(\tau)$ and $\varphi''(\tau)$ in powers of τ. As first mentioned in a previous paper [15], the value of the second derivative of the chemical potential with respect to the temperature on the critical isochore remains finite in the critical point [$(\partial^2\mu/\partial\tau^2)_{\rho=\rho_c} \sim \tau^{\gamma-1-\alpha} \sim \tau^{0.1}$], and only its third derivative tends to infinity. This resolves the question of what quantity diverges in the well-known expression for the isochorous heat capacity

$$\frac{C_v}{T} = \frac{1}{\rho}\left(\frac{\partial^2 P}{\partial \mathrm{T}^2}\right)_\rho - \left(\frac{\partial^2 \mu}{\partial \mathrm{T}^2}\right)_\rho \tag{17}$$

The investigated quantities behave quite differently on the critical isotherm. In this case when $|B_2| \gtrsim |c|$, asymmetric corrections become of the same order as the nonasymptotic terms ($\gamma + \beta - 1 \approx \Delta \approx 0.5$). Thus in the description of the experimental P–V–T data as well as of K_T, C_p, and C_v in the wide range of $\Delta\rho$ in terms of a single equation of state, both nonasymptotic and nonasymmetric terms should be taken into account. As for the second derivative of the chemical potential with respect to temperature, it depends nonanalytically on the density. It tends to infinity at $\rho = \rho_c$ and $T = T_c$ even in the asymptotic approximation without taking into account the asymmetry. Namely, from Eq. (17), with the help of the known thermodynamic equality $(1/\mathrm{T})(\partial C_v/\partial v) = (\partial^2 P/\partial \mathrm{T}^2)_v$, we obtain

$$\frac{v}{T}\left(\frac{\partial^2 C_v}{\partial \mathrm{T}^2}\right)_T = \frac{\partial}{\partial v}\left[\left(\frac{\partial^2 \mu}{\partial \mathrm{T}^2}\right)_v\right] \tag{17a}$$

i.e., the quantity $(\partial^2\mu/\partial\tau^2)$ behaves as $|\Delta\rho|^{[(-\alpha+\beta)/\beta]}$ while approaching the critical point along the line $T = T_c$ (see Table II). Asymmetric corrections in this case remain of the same order as the nonasymptotic terms.

4. THE ASYMMETRIC SCALED EQUATION OF STATE

Unfortunately, the Pokrovsky transformation in the form given by Eqs. (1), (5), (10), and (11) does not make it possible to perform an

Table II. Behavior of Various Thermodynamic Values in the Critical Region with Account of Asymmetry

Thermodynamic quantity	Condition	Pokrovsky transformation, Eqs. (1) and (5)	Ley-Koo and Green analysis [16]	"Asymmetric" Eqs. (26) and (32)
$\Delta\mu$	$\rho=\rho_c$	$\tau^{\gamma+1-\alpha}$	$\tau^{\gamma+1-\alpha}+\tau^{\gamma+1}$	$\tau^{\gamma+1-\alpha}$
	$T=T_c$	$\pm\lvert\Delta\rho\rvert^{\delta}\pm\lvert\Delta\rho\rvert^{\delta+(\Delta/\beta)}$ $+\lvert\Delta\rho\rvert^{\delta+[(\gamma+\beta-1)/\beta]}$	—[a]	$\pm\lvert\Delta\rho\rvert^{\delta}\pm\lvert\Delta\rho\rvert^{\delta+(\Delta/\beta)}$ $+\lvert\Delta\rho\rvert^{\delta+[(\gamma+\beta-1)/\beta]}$
	$T=T_S$	—[a]	$\lvert\tau_S\rvert^{2\beta\delta-1}+\lvert\tau_S\rvert^{2\beta\delta-1+\Delta}$	$\lvert\tau_S\rvert^{\beta\delta+\Delta}+\lvert\tau_S\rvert^{2\beta\delta-1}+\lvert\tau_S\rvert^{2\beta\delta+2\Delta}$ $+\lvert\tau_S\rvert^{2\beta\delta-1+\Delta}$
$(T_c/P_c)(\rho C_v/T)$	$\rho=\rho_c$	$\tau^{-\alpha}+\tau^{-\alpha+\Delta}+\tau^{\gamma-2\alpha}+\tau+\text{const}$	$\tau^{-\alpha}+\tau^{-\alpha+\Delta}+\tau+\text{const}$	$\tau^{-\alpha}+\tau^{-\alpha+\Delta}+\tau^{-\gamma-\alpha}+\tau+\text{const}$
	$T=T_c$	$\lvert\Delta\rho\rvert^{-\alpha/\beta}+\lvert\Delta\rho\rvert^{(-\alpha+\Delta)/\beta}$ $\pm\lvert\Delta\rho\rvert^{[-\alpha+(\gamma+\beta-1)]/\beta}$	—[a]	$\lvert\Delta\rho\rvert^{-\alpha/\beta}+\lvert\Delta\rho\rvert^{(-\alpha+\Delta)/\beta}$ $\pm\lvert\Delta\rho\rvert^{[-\alpha+(\gamma+\beta-1)]/\beta}$
	$T=T_S$	—[a]	$\lvert\tau_S\rvert^{-\alpha}+\lvert\tau_S\rvert^{-\alpha+\beta}+\lvert\tau_S\rvert^{-\alpha+\Delta}$ $+\lvert\tau_S\rvert+\text{const}$	$\lvert\tau_S\rvert^{-\alpha}+\lvert\tau_S\rvert^{-\alpha+\Delta}+\lvert\tau_S\rvert^{1-2\alpha-\beta}$ $+\lvert\tau_S\rvert^{1-\alpha-\beta}+\lvert\tau_S\rvert+\text{const}$
$P_c(\rho^2/\rho_c^2)K_T$	$\rho=\rho_c$	$\tau^{-\gamma}+\tau^{-\gamma+\Delta}+\tau^{-\alpha}$	$\tau^{-\gamma}+\tau^{-\gamma+\Delta}+\tau^{-\gamma+2\Delta}+\tau^{-\alpha}$	$\tau^{-\gamma}+\tau^{-\gamma+\Delta}$
	$T=T_c$	$\lvert\Delta\rho\rvert^{-\gamma/\beta}+\lvert\Delta\rho\rvert^{(-\gamma+\Delta)/\beta}$ $\pm\lvert\Delta\rho\rvert^{[-\gamma+(\gamma+\beta-1)]/\beta}$	—[a]	$\lvert\Delta\rho\rvert^{-\gamma/\beta}+\lvert\Delta\rho\rvert^{(-\gamma+\Delta)/\beta}$ $\pm\lvert\Delta\rho\rvert^{[-\gamma+(\gamma+\beta-1)]/\beta}$
	$T=T_S$	—[a]	$\lvert\tau_S\rvert^{-\gamma}+\lvert\tau_S\rvert^{-\gamma+\Delta}+\lvert\tau_S\rvert^{\beta-1}$ $+\lvert\tau_S\rvert^{-\gamma+2\Delta}$	$\lvert\tau_S\rvert^{-\gamma}+\lvert\tau_S\rvert^{-\gamma+\Delta}+\lvert\tau_S\rvert^{\beta-1}+\lvert\tau_S\rvert^{-\gamma+2\Delta}$

[a] Asymptotics were not analyzed.

analytical integrating in the variables ρ and T. This means that within the framework of this approach, it is not possible to obtain in the parametric form the rigorous equation for a free energy and, consequently, for the pressure of fluids. Nevertheless, this approach yields a rather simple and physically justified approximation of such an equation.

To obtain an asymmetric equation of state for real fluids, we assume that $v = 0$ in Eqs. (1), (3), and (5) and consider parameter u as a function of Γ and θ. As all the scaling equations are analytic functions of the variable θ in the parametric presentation, the function $\tilde{U}(\Gamma, \theta)$ can be represented in the form of a series in even powers of θ:

$$\tilde{U}(\Gamma, \theta) = \Gamma^{\Delta_A} \sum_{i=1}^{m} b_i \theta^{2(i-1)}. \tag{18}$$

We have already taken into account here that the influence of the asymmetry is due to the appearance of the even terms in the chemical potential with respect to $\Delta\rho$. By substitution of the expansion given by Eq. (18) into Eq. (5a) instead of the parameter u and limiting of the terms, we obtain the following expression for the chemical potential of a real asymmetric system:

$$\Delta\mu(\Gamma, \theta) = \Delta\mu_{\mathrm{LG}}(\Gamma, \theta) + \Gamma^{\Delta_{\mathrm{A}}+1}[b_1 + (b_2 - b_1 b^2)\theta^2 + (b_3 - b_2 b^2)\theta^4] \tag{19}$$

The exponent Δ_{A} and the expansion constants b_1, b_2, and b_3 in Eq. (19) can be determined by identifying the asymmetric terms arising from Eq. (19) in the isothermic compressibility K_{T}^{*} and the heat capacity C_{v} with the corresponding terms in Eqs. (14) and (15) which have been obtained from the rigorous Pokrovsky transformations. For this purpose we differentiate Eq. (19) with respect to $\Delta\rho$ and compare the resulting exponent of Γ with the corresponding exponent in Eq. (14). From the condition of equality of these exponents of the asymmetric terms, we obtain

$$\Delta_{\mathrm{A}} = 2\gamma + 2\beta - 2 \tag{20}$$

To trace a connection among the coefficients b_1, b_2, and b_3 and to obtain the general form of a free energy with account of the asymmetry, we integrate Eq. (15) twice over τ [the coupling equations between the variable (Γ, θ) and the variable (ρ, T) in the considered approximation are being set by Eqs. (7) and (8)]. We thus obtain the following expression for the free energy per unit volume:

$$\rho F = P_{\mathrm{c}} \left[\psi_{\mathrm{LG}}(\Gamma, \theta) + \psi_{\mathrm{AS}}(\Gamma, \theta) + \frac{\rho}{\rho_{\mathrm{c}}} M(\tau) + \varphi(\tau) \right] \tag{21}$$

where the singular part of a free energy due to asymmetry has the form

$$\psi_{\mathrm{AS}} = \frac{k}{b^2}\Gamma^{2\gamma+3\beta-1}\theta[h_1 + h_2\theta^2 + h_3\theta^4] \tag{22}$$

To pass from the free energy to the chemical potential $\mu = (\partial\rho F/\partial\rho)_{\mathrm{T}}$, we make use of the equality $\Delta\mu = (\partial\psi/\partial\Delta\rho)_\tau$. Then we obtain from Eqs. (19) and (22) with Eqs. (7) and (8),

$$\begin{gathered} h_1 = b_1 b^2, \qquad h_2 = \frac{b_2 b^2 - b_1 b^4(1 + 2e - 2\beta)}{3}, \\ h_3 = b^2\frac{1-2\beta}{10\beta - 2e}[2h_1(e-\beta)(1-2\beta)b^2 + 2h_2(e-3\beta)] \end{gathered} \tag{23}$$

The parameter b_3 in Eq. (19) turns out to be related to the coefficients b_1 and b_2 by

$$b_3 = b_1 b^4(e_1 - e_2) + b_2 b^2(1 - e_2) \tag{24}$$

Introducing a new notation for b_1 and b_2,

$$b_1 = d, \qquad b_2 = (f + d)b^2 \tag{25}$$

we finally obtain Eqs. (19)–(23), asymmetric equations for a chemical potential and the singular part of a free energy:

$$\Delta\mu(\Gamma,\theta) = \Delta\mu_{\mathrm{LG}}(\Gamma,\theta) + \Gamma^{2\gamma+2\beta-1}[d(1 + e_1 b^4\theta^4) + f b^2\theta^2(1 + e_2 b^2\theta^2)] \tag{26}$$

$$\begin{aligned} \psi(\Gamma,\theta) = \psi_{\mathrm{LG}}(\Gamma,\theta) + k\Gamma^{2\gamma+3\beta-1}\theta\Big\{ & d + \frac{1}{3}[f - 2d(e-\beta)]b^2\theta^2 \\ & + \frac{1-2\beta}{5-2e}[de_1 + fe_2]b^4\theta^4\Big\} \end{aligned} \tag{27}$$

Here d and f are new nonuniversal constants, the functions $\Delta\mu_{\mathrm{LG}}(\Gamma,\theta)$ and $\psi_{\mathrm{LG}}(\Gamma,\theta)$ are calculated in accordance with the corresponding expressions for a symmetric lattice-gas model [Eqs. (6) and (9)], and the values e, e_1, and e_2 depend only on the critical exponents and have the following form:

$$\begin{aligned} e &= 2\gamma + 2\beta - 1 \\ e_1 &= \frac{2(5-2e)(e-\beta)(3-2e)}{3(10\beta - 2e)} \\ e_2 &= \frac{2(5-2e)(e-3\beta)}{3(10\beta - 2e)} \end{aligned} \tag{28}$$

The asymmetric equation for the pressure $P = -\rho^2(\partial F/\partial\rho)_T$ of a real fluid becomes

$$P = P_c\left[\frac{\rho}{\rho_c}\Delta\mu(\Gamma, \theta) - \psi(\Gamma, \theta) - \varphi(\tau)\right] \tag{29}$$

where the functions $\Delta\mu(\Gamma, \theta)$ and $\psi(\Gamma, \theta)$ are calculated with the help of Eqs. (26) and (27). The function $\varphi(\tau)$ is analytic and can be represented by an expansion of the form

$$\varphi(\tau) = -1 + f_1\tau + f_2\tau^2 + f_3\tau^3 + f_4\tau^4 \tag{30}$$

The relation between the parameter (Γ, θ) and the parameter $(\tau, \Delta\rho)$ has the same form as for the symmetric lattice-gas model [$v = 0$ in Eqs. (10) and (11)] with the exception of the term $\sim B_3\tau$, which is to be added to Eq. (8):

$$\tau = \Gamma(1 - b^2\theta^2) \tag{31}$$

$$\Delta\eta = \Delta\rho + B_3\tau = k\Gamma^\beta\theta \tag{32}$$

The coefficient B_3 corresponds to the slope of the rectilinear diameter on the coexistence curve in the scaled Eq. (12). This term is necessary so as to take into account the term $\sim\Delta N^3\tau$ in the effective Hamiltonian, which disturbs its symmetry with respect to ΔN. This term can be eliminated by a formal transformation $\Delta N \rightarrow \Delta N + \text{const}$ [11], which makes it possible to pass from the variable $\Delta\rho$ to the new variable $\Delta\eta = \Delta\rho + \text{const}\cdot\tau$ in Eqs. (26) and (27) without changing the form of the thermodynamic potential given by Eq. (21).

It can be shown that Eqs. (21) and (26)–(32) lead to the same results in the behavior of the thermodynamic quantities as those of the Pokrovsky rigorous transformations given by Eqs. (1) and (5). They are also in good agreement with the results of the renormalization-group analysis carried out by Ley-Koo and Green [16]. For this, let us consider the behavior of the main thermodynamic quantities along the coexistence curve, the equation for which can be found from the conditions

$$\begin{aligned} P(\Gamma_1, \theta_1) - P(\Gamma_2, \theta_2) &= 0 \\ \mu(\Gamma_1, \theta_1) - \mu(\Gamma_2, \theta_2) &= 0 \\ \tau_S - \tau(\Gamma_1, \theta_1) &= 0 \\ \tau_S - \tau(\Gamma_2. \theta_2) &= 0 \end{aligned} \tag{33}$$

Here $\tau_S = (T_S - T_c)/T_c$ (T_S is a temperature of saturation), and Γ_1, θ_1 and Γ_2, θ_2 correspond to the parameter values Γ and θ on the liquid and gas branches of the coexistence curve, reprectively. Let us consider the relations given by Eq. (33) as that of the implicitly defined functions

$$\begin{aligned}\theta_1 &= \theta_1(\Gamma_1 \mid x_1, x_2, x_3)\\ \theta_2 &= \theta_2(\Gamma_2 \mid x_1, x_2, x_3)\end{aligned} \tag{34}$$

$x_1 = c/a$, $x_2 = d/a$, and $x_3 = f/a$ [a, c, d, and f are nonuniversal constants in Eqs. (26) and (27)]. Then, expanding θ_1 and θ_2 in powers of x_i in the vicinity of the point $x_i = 0$ [$\theta_{1,2} = \pm 1$, $\Gamma_1 = \Gamma_2 = |\tau|/(b^2-1)$], we obtain from Eq. (33) with Eqs. (6), (9), and (26)–(31) in the linear approximation in θ,

$$\theta_{1,2} = \pm 1 \pm a_1 \tau^{\Delta} + (a_2 + a_3)\Gamma^{1-\alpha-\beta} \tag{35}$$

where

$$a_1 = \frac{c}{2a}, \qquad a_2 = \frac{d}{a} b^2 \left(b^2 e_1 \frac{2-e+\beta}{5-2e} + \frac{e-\beta}{3} \right),$$

$$a_3 = \frac{f}{a} b^2 \left(b^2 e_2 \frac{2-e+\beta}{5-2e} + \frac{1}{3} \right)$$

Let us rewrite Eq. (35) in a slightly different form, namely, replacing Γ with $|\tau_S|/(b^2-1)$ in accordance with Eq. (31). After substitution into Eq. (32), we obtain the following equation for the density on the coexistence curve:

$$\Delta\rho = \pm \frac{k(-\tau_S)^{\beta}}{(b^2-1)^{\beta}} \pm \frac{kc(-\tau_S)^{\beta-\Delta}}{2a(b^2-1)^{\beta+\Delta}} + \frac{k(a_2+a_3)(-\tau_S)^{1-\alpha}}{(b^2-1)^{1-\alpha}} + B_3(-\tau_S) \tag{36}$$

Comparing this result with the scaled equation for the coexistence curve, we obtain

$$B_0 = \frac{k}{(b^2-1)^{\beta}} \tag{37}$$

$$B_1 = \frac{kc}{2a(b^2-1)^{\beta+\Delta}} \tag{38}$$

The parameters d and f are related to the amplitude of the "singular" diameter by the following expression:

$$B_2 = -\frac{kb^4}{a(b^2-1)^{1-\alpha}} \left[\frac{e-\beta-2}{5-2e}(de_1 + fe_2) - \frac{d(e-\beta)+f}{3b^2} \right] \tag{39}$$

Next we determine the behavior of the maxima of the isothermal compressibility $K_T^* = P_c(\rho^2/\rho_c^2)K_T$, the equation for which can be obtained from the condition

$$\frac{\partial}{\partial \Delta\rho}\left[\left(\frac{\partial\rho}{\partial\mu}\right)_T\right]_T = 0 \quad \text{or} \quad \left(\frac{\partial^2 \Delta\mu}{\partial \Delta\rho^2}\right)_\tau = 0 \tag{40}$$

Differentiating Eq. (26) twice with respect to $\Delta\rho$ and after simple but tiresome algebraic transformations in a linear approximation in θ, we obtain from the condition given by Eq. (40),

$$\theta_{\max K_T^*} = -b^2 \frac{d(e-\beta)+f}{3\alpha(\gamma b^2 - 1)} \Gamma^{1-\alpha-\beta} \tag{41}$$

After substitution of this expression into Eq. (32) and using Eqs. (31) and (39), we finally obtain

$$\Delta\rho_{\max K_T^*} = -\frac{B_2}{(\gamma b^2-1)}\left[1 + \frac{kb^2}{aB_2}\frac{(de_1+fe_2)(e-\beta-2)}{(b^2-1)^{1-\alpha}(5-2e)}\right]\tau^{1-\alpha} - B_3\tau \tag{42}$$

Comparing this equation with Eq. (16) we see that, contrary to the Pokrovsky transformations, the sign before the term $\sim\tau^{1-\alpha}$ depends not only on that of B_2, but also on the numerical value and the signs of the parameters a, d, and f. In addition, as there is also the term $\sim\tau$ in Eq. (42), the maxima line may have a different form, which is determined by the whole combination of constants in Eqs. (26) and (32).

The expressions obtained make it possible also to evaluate the behavior of the coefficient of the isothermal compressibility $\rho^2 K_T = (\partial\rho/\partial\mu)_T$ and the isochoric heat capacity $(\rho C_v/\mathrm{T}) = -(\partial^2 F/\partial T^2)_\rho$ on the coexistence curve. For this, let us differentiate Eq. (26) with respect to density and differentiate Eq. (21) with respect to temperature twice. Then after substitution of the value of the parameter θ on the coexistence curve given by Eq. (35) in the expressions obtained, and keeping the leading terms in Γ, we obtain, finally, for the isothermal compressibility and for the heat capacity along the coexistence curve,

$$\begin{aligned} \rho^2 K_T &= \Gamma_0|\tau_S|^{-\gamma}(1 + \Gamma_1|\tau_S|^{\Delta} + \Gamma_2|\tau_S|^{\gamma+\beta-1} + \Gamma_3|\tau_S|^{2\Delta}) \\ \frac{\rho C_v}{T_S} &= A_0|\tau_S|^{-\alpha}(1 + A_1|\tau_S| + A_2|\tau_S|^{1-\alpha-\beta} + A_3|\tau_S|^{1-\beta} + A_4|\tau_S|) + A_5 \end{aligned} \tag{43}$$

The behavior of the other thermodynamic quantities on the coexistence curve, as well as on the critical isochor ($\theta = 0$, $\Gamma = \tau$) and on the critical isotherm [$\theta = \pm 1/b$, $\Gamma = (|\Delta\rho|^B/k)^{1/\beta}$], can be evaluated in a similar way.

The results of this analysis, together with the results obtained both from the Pokrovsky transformations and from the analysis performed by Ley-Koo and Green [16], are presented in Table II. It is evident from Table II that the equations obtained give asymptotics, which coincide with those obtained by other methods, on practically all selected lines. Thus, e.g., the Pokrovsky transformations and the equations obtained identically described the behavior of the chemical potential and, consequently, that of its second derivative $(\partial^2\mu/\partial T^2) \sim \tau^{\gamma-1-\alpha}$ on the critical isochore as a function of temperature. The asymptotics of all investigated quantities which depend on the density on a critical isotherm also fully coincide. This fact, as mentioned above, is particularly important for the investigation of the influence of the asymmetry of a real fluid with respect to the critical isochore. The singularities of the behavior of the isothermal compressibility on the coexistence curve, depending on temperature, coincide identically. Some slight differences manifest themselves in the temperature dependence of the heat capacity C_v both on the critical isochore (terms $\sim\tau^{\gamma-2\alpha}$ and $\sim\tau^{\gamma-\alpha}$) and on the coexistence curve (terms $\sim\tau^{-\alpha+\beta}$, $\sim\tau^{1-2\alpha-\beta}$, and $\sim\tau^{1-\alpha-\beta}$) and also of the isothermal compressibility on the critical isochore (term $\sim\tau^{-\alpha}$ appears only from the Pokrovsky transformation and from the analysis performed by Ley-Koo and Green [16], and it is absent in the "asymmetric" equation). The terms mentioned are substandially smaller than the leading asymptotic terms in the corresponding equations. In addition, they are commensurable with terms proportional to $\sim\tau$, which arise while expanding the regular part of the thermodynamic potential in powers of τ.

Thus we see that the equations obtained provide an adequate description of the singularities in the behavior of all thermodynamic quantities due to the asymmetry of a real fluid.

It is also necessary to emphasize that approaching the critical point (or in the limit of d and $f \to 0$), they reduce to the rigorous scaled equations. Such a structure of the equations obtained makes it possible to use them not only for calculation of the thermodynamic properties of pure substances, but also for that of binary mixtures in the critical region. In this case it is sufficient in the isomorphous equation of state described in Ref. 7, to use the function $\psi(\Gamma, \theta)$, calculated with the help of Eq. (27).

5. APPLICATION

To test quantitatively the effectiveness and the accuracy of the equations obtained, we have used the asymmetric equation of state for a real fluid for the description of the P, V, T data for steam in a broad range around the critical point [17]. The parameters in the equation were deter-

Table III. Parameters in the Equation of State Given by Eq. (29) of Steam in the Critical Region

Parameter	Mean value	95% confidence interval
k	1.404	— (fixed)
B_4	−0.45	— (fixed)
a	22.94	±0.15
c	−4.12	±0.36
d	4.43	±0.70
f	−8.89	±1.1
f_1	−7.812	±0.012
f_2	18.3	±0.51
f_3	10.1	±4.4
f_4	−40.2	±13.0

mined from a fit to the experimental P, V, T data of Rivkin and co-workers [18–20]. For this purpose we use the algorithm proposed by Berestov and Malyshev [21], which makes it possible to determine the parameters and their confidence limits and also to test the adequacy of the model with the help of the Fisher criterion $F_{0.95}(N_1, N_2)$ (N is the number of free parameters, and N_2 is the number of points). The values of the critical exponents α, β, and Δ were fixed at $\alpha = 0.11$, $\beta = 0.34$, and $\Delta = 0.45$, and the critical exponents were calculated according to the known scaling-theory correlations ($\gamma = 2 - \alpha - 2\beta$, $\beta\delta = \gamma + \beta$). The values of the critical tem-

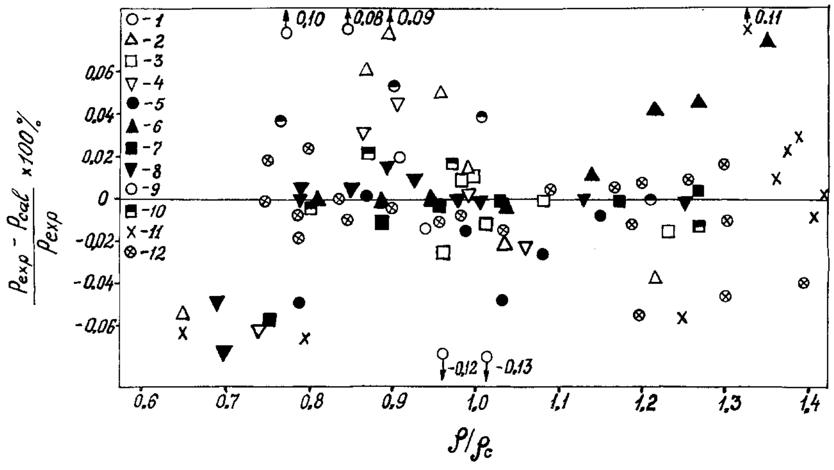

Fig. 1. Deviation of experimental values of pressure in the critical region of steam from calculated values: (1) $T/T_c = 1.20$; (2) 1.16; (3) 1.12; (4) 1.08; (5) 1.07; (6) 1.06; (7) 1.04; (8) 1.03; (9) 1.02; (10) 1.01; (11) 1.00; (12) 0.99.

perature and density were assumed to be equal to $T_c = 647.067$ K and $\rho = 322.778\ \mathrm{kg \cdot m^{-3}}$, in agreement with the values determined by Levelt-Sengers et al. [22]. The critical pressure $P_c = 22.07 \pm 0.09$ MPa was found from a fit to the experimental data. The values of the parameters k and B_3 were determined from a fit to the data on the coexistence curve [23]. The values of the parameters are listed in Table III, and the results of the calculations are shown in Fig. 1. It is seen from the figure that in the range of temperatures from the saturation line ($T = T_s$) to $T = 1.2T_c$ and for the densities $0.65 \leqslant (\rho/\rho_c) \leqslant 1.4$, the discrepancies between the experimental and the calculated values of the pressure average 0.05–0.04%, which is within the experimental error. In addition, all the optimized parameters in Eqs. (26)–(32) are statistically significant (see Table III) and the equation obtained adequately describes the experimental data [$F(9, 90) = 1.576$] in the range mentioned above. This yields strong evidence for the physical and methodical reliability of the proposed equations.

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