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# A Universal Representation of the Thermodynamic Properties of Fluids in the Critical Region[1]

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To characterize the behavior of the thermodynamic properties of systems near a critical point, systems are grouped into universality classes. Systems within a universality class have the same universal critical exponents and scaling functions. Specifically, fluids are expected to belong to the universality class of three-dimensional Ising-like systems for which the universal quantities have been calculated with considerable accuracy. A scaled fundamental equation is presented which incorporates these theoretical predictions. Results obtained for various technologically important fluids, namely ordinary steam, heavy steam, ethylene, and isobutane, are discussed.

**KEY WORDS:** critical-point universality; critical region; equation of state; ethylene; isobutane; scaling laws; steam; thermodynamic properties.

## 1. INTRODUCTION

The accurate characterization of the near-critical region of fluids has become of increasing importance for the following reasons. First of all, the critical parameters are used as reduction parameters in many engineering equations. Their values are more often inferred from analysis of near-critical behavior than from direct measurements. Second, working fluids, such as steam in power generation and isobutane in binary geothermal power cycles, operate in supercritical power cycles. Third, in the climatic

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conditions of the U.S., the custody transfer of important chemicals such as ethylene and carbon dioxide may occur in near-critical conditions. Lastly, supercritical fluids such as carbon dioxide and ethylene are used as extractants.

An accurate representation of the thermodynamic behavior of near-critical fluids is complicated by the fact that the thermodynamic surface of fluids becomes nonanalytic at the critical point. The singular behavior is due to the fact that the critical point is a point of marginal thermodynamic stability, which leads to the presence of large-scale density fluctuations in the vicinity of the critical point.

During the past two decades considerable progress has been made in our scientific understanding of the nature of critical-point phase transitions. The mathematical character of the anomalous critical behavior is expected to be universal, i.e., the same for large classes of systems. Specifically, the hypothesis of critical-point universality asserts that fluids near the gas–liquid critical point belong to the universality class of Ising-like systems, i.e., three-dimensional systems with a one-dimensional order parameter and with short-range forces. Many detailed theoretical predictions have become available for this universality class, in particular from the renormalization-group theory of critical phenomena applied to spin systems. Guided by the analogy between Ising model and lattice gas, it is possible to apply the theoretical predictions to fluids as well. Using this approach, we have formulated a nonanalytic fundamental equation for fluids in the critical region that incorporates the theoretically predicted singular behavior.

In this paper we discuss the theoretical foundations of this fundamental equation and summarize our results obtained to date for technologically important fluids.

## 2. THEORETICAL PREDICTIONS

The modern theoretical predictions for the properties of systems near a critical point are based on the renormalization-group theory of critical phenomena. This theory was introduced by Wilson [1], for which he received the Nobel Prize in 1982. As shown by Wegner, this theory implies that the thermodynamic potential of a spin system near the Curie point can be represented by an expansion of the form [2, 3]

$$F = F_0 + |u_t|^{\beta(\delta+1)} f_0(x) + u_1 |u_t|^{\beta(\delta+1)+\Delta} f_1(x) + \cdots \tag{1}$$

with

$$x = u_h / |u_t|^{\beta\delta} \tag{2}$$

Here $\beta$ and $\delta$ are the exponents of the critical power laws that characterize the asymptotic behavior of the order parameter along the coexistence boundary and of the ordering field along the critical isotherm; the exponent $\Delta$ accounts for the nonanalytic behavior of the first correction to the asymptotic power law behavior. The variables $u_t$ and $u_h$ are so-called relevant scaling fields, which vanish at the critical point, while $u_1$ is the first irrelevant scaling field that remains finite at the critical point. For spin systems, the thermodynamic potential $F$ is identified with the Gibbs free energy divided by $k_B T$, where $k_B$ is Boltzmann's constant and $T$ the temperature. The scaling fields $u_t$, $u_h$, and $u_1$ and the background function $F_0$ are assumed to be analytic functions of the physical fields, temperature $T$, and magnetic field $H$, or, equivalently, $1/k_B T$ and $H/k_B T$. The critical exponents $(\beta, \delta, \Delta)$ and the scaling functions $(f_0, f_1)$ should be the same for all systems within a universality class; system-dependent quantities only appear in the expansion of the scaling fields and of the background function $F_0$. Accurate theoretical predictions for the critical exponents for the universality class of three-dimensional Ising-like systems are currently available [4]. These theoretical values are in good agreement with available experimental evidence [5–8]. For the purpose of our work we have adopted the universal exponent values

$$\beta = 0.325, \qquad \delta = 4.82, \qquad \Delta = 0.5 \tag{3}$$

There exists also a considerable amount of theoretical information for the universal scaling function $f_0$, but less for the universal correction-to-scaling function $f_1$.

For symmetric spin systems, $u_h$ reduces to $H/k_B T$ itself, while $u_t$, $u_1$, and $F_0$ are functions of the temperature only [2]. In that case the thermodynamic potential $F$ is invariant under the inversion of the magnetic field. In the more general case of nonsymmetric spin systems, to be considered here, the scaling fields and $F_0$ become functions of both $1/k_B T$ and $H/k_B T$ [2, 9]. The scaling functions $f_0$ and $f_1$, being universal, remain even functions of the variable $x$; odd scaling functions do appear in the expansion (1), but they are associated with higher order terms [9, 10].

## 3. SCALED THERMODYNAMIC POTENTIAL FOR FLUIDS

A procedure for applying the Wegner expansion (1) to fluids near the gas–liquid critical point was proposed by Ley-Koo and Green [11]. They assume an analogy between the grand-canonical partition function of a fluid and the canonical partition function of a spin system as is known to exist for the lattice gas [12, 13]. Accordingly, they identify the Gibbs function with the pressure $P$ and the magnetic field with the chemical potential $\mu$. Specifically, we consider the potential $P/T$ as a function of $1/T$ and $\mu/T$ and write the Wegner expansion (1) in the form

$$\tilde{P} = \tilde{P}_0(\tilde{T}, \tilde{\mu}) + |u_t|^{\beta(\delta+1)} f_0(x) + u_1 |u_t|^{\beta(\delta+1)+\Delta} f_1(x) \tag{4}$$

truncating the expansion after the first correction-to-scaling term. Here we introduce the reduced quantities

$$\tilde{P} = \frac{P}{T}\frac{T_c}{P_c}, \qquad \tilde{T} = -\frac{T_c}{T}, \qquad \tilde{\mu} = \frac{\mu}{T}\frac{\rho_c T_c}{P_c}, \qquad \tilde{\rho} = \frac{\rho}{\rho_c}, \qquad \tilde{U} = \frac{U}{P_c V} \tag{5}$$

where $\mu$ is the chemical potential, $\rho$ the density, $V$ the volume, and $U$ the internal energy, while $T_c$, $P_c$, and $\rho_c$ refer to the values of $T$, $P$, and $\rho$ at the critical point. In addition, we define the variables

$$\Delta\tilde{T} = \tilde{T} + 1, \qquad \Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_0(\tilde{T}) \tag{6}$$

chosen such that $\Delta\tilde{T} = 0$ and $\Delta\tilde{\mu} = 0$ at the critical point. The functions $\tilde{\mu}_0(\tilde{T})$ and $\tilde{P}_0(\tilde{T}, \tilde{\mu})$ are analytic functions, which will be expanded around their values at the critical point in powers of $\Delta\tilde{T}$, and of $\Delta\tilde{T}$ and $\Delta\tilde{\mu}$, respectively. In the range of validity of the fundamental equation (4), we find that the expansions can be truncated as

$$\tilde{\mu}_0(\tilde{T}) = \tilde{\mu}_c + \sum_{i=1}^{3} \tilde{\mu}_i (\Delta\tilde{T})^i \tag{7}$$

$$\tilde{P}_0(\tilde{T}, \tilde{\mu}) = 1 + \sum_{i=1}^{3} \tilde{P}_i (\Delta\tilde{T})^i + \Delta\tilde{\mu} + \tilde{P}_{11}(\Delta\tilde{T})(\Delta\tilde{\mu}) \tag{8}$$

The scaling fields $u_t$, $u_h$, and $u_1$ are analytic functions of $\Delta\tilde{T}$ and $\Delta\tilde{\mu}$. Except for a system-dependent proportionality factor, we obtain in lowest order [11, 14]

$$u_h = \Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_0(\tilde{T}) \tag{9}$$

$$u_t = \Delta\tilde{T} + c\,\Delta\tilde{\mu} \tag{10}$$

while $u_1$ can be approximated by a constant. At coexistence $u_h = 0$ and $\tilde{\mu}_0(\tilde{T})$ is to be interpreted as the saturation chemical potential curve for $\Delta\tilde{T} < 0$ or its analytic extension for $\Delta\tilde{T} > 0$. The system-dependent constant $c$ in (10) accounts for the mixing of the $\Delta\tilde{T}$ and $\Delta\tilde{\mu}$ variables in the effective scaling field $u_t$ for nonsymmetric systems.

The potential $\tilde{P}$ satisfies the differential relation

$$d\tilde{P} = \tilde{U}\,d\tilde{T} + \tilde{\rho}\,d\tilde{\mu} = \left(\tilde{U} + \tilde{\rho}\frac{d\tilde{\mu}_0}{d\tilde{T}}\right)d(\Delta\tilde{T}) + \tilde{\rho}\,d(\Delta\tilde{\mu}) \tag{11}$$

This relation enables one to obtain expressions for the various thermodynamic properties from the potential $\tilde{P}$ [14, 15].

In order to specify the fundamental equation, we need explicit expressions for the universal scaling functions $f_0(x)$ and $f_1(x)$ in (4). However, to avoid nonanalyticities in the one-phase region away from the critical point, it appears necessary to introduce a coordinate transformation from the scaling fields $u_h$ and $u_t$ to a new set of (parametric) variables $r$ and $\theta$. These variables are such that $r$ measures, in some sense, distances from the critical point, while $\theta$ measures locations along contours of constant $r$. Since the nonanalytic behavior of $\tilde{P}$ manifests itself at the critical point ($r = 0$), it is then assumed that $\Delta\tilde{P} = \tilde{P} - \tilde{P}_0(\tilde{T}, \tilde{\mu})$ is analytic in $\theta$ and only nonanalytic in $r$. The transformation commonly used is [13]

$$u_h = r^{\beta\delta}a\theta(1 - \theta^2) \tag{12}$$

$$u_t = r(1 - b^2\theta^2) \tag{13}$$

where $a$ and $b$ are constants. At coexistence $u_h = 0$ and the values $\theta = \pm 1$ correspond to the two branches of the coexistence curve. It follows that the potential $\tilde{P}$ must depend on $r$ and $\theta$ in such a way that

$$\frac{\partial(\Delta\tilde{P})}{\partial u_h} = r^{\beta}\left[m_0(\theta) + r^{\Delta}m_1(\theta)\right] \tag{14}$$

Since $\Delta\tilde{P}$ is even in $u_h$, $\partial(\Delta\tilde{P})/\partial u_h$ must be odd in $u_h$ and hence odd in $\theta$. The simplest approximation, which turns out to be adequate, is to assume that $m_0(\theta)$ and $m_1(\theta)$ are proportional to $\theta$,

$$m_0(\theta) = k_0\theta \tag{15}$$

$$m_1(\theta) = k_1\theta \tag{16}$$

The approximation (15) was originally introduced by Schofield *et al.* [16] and defines the so-called linear-model scaled equation of state for the asymptotic critical behavior [13]. The generalization (16) of the linear-

**Table I.** Coefficients for $p_i(\theta) = p_{0i} + p_{2i}\theta^2 + p_{4i}\theta^4$

$$p_{00} = +\frac{\beta(\delta-3) - b^2\beta(\delta-1)(2-\beta\delta-\beta)}{2b^4\beta(\delta+1)(\beta\delta+\beta-1)(2-\beta\delta-\beta)}$$

$$p_{20} = -\frac{\beta(\delta-3) - b^2(2\beta\delta-1)(2-\beta\delta-\beta)}{2b^2(\beta\delta+\beta-1)(2-\beta\delta-\beta)}$$

$$p_{40} = +\frac{2\beta\delta-3}{2(2-\beta\delta-\beta)}$$

$$p_{01} = +\frac{\beta(\delta-3) - 3\Delta - b^2(\beta\delta-\beta-\Delta)(2-\beta\delta-\beta-\Delta)}{2b^4(\beta\delta+\beta+\Delta)(\beta\delta+\beta-1+\Delta)(2-\beta\delta-\beta-\Delta)}$$

$$p_{21} = -\frac{\beta(\delta-3) - 3\Delta - b^2(2\beta\delta-1)(2-\beta\delta-\beta-\Delta)}{2b^2(\beta\delta+\beta-1+\Delta)(2-\beta\delta-\beta-\Delta)}$$

$$p_{41} = +\frac{2\beta\delta-3}{2(2-\beta\delta-\beta+\Delta)}$$

model approximation to the first correction-to-scaling term was introduced by Balfour *et al.* [17]. With the equations for $m_0(\theta)$ and $m_1(\theta)$, the scaled fundamental equation is completely specified and the singular part $\Delta\tilde{P}$ of the potential becomes

$$\Delta\tilde{P} = ar^{\beta(\delta+1)}\left[k_0 p_0(\theta) + r^{\Delta}k_1 p_1(\theta)\right] \tag{17}$$

with $p_i(\theta) = p_{0i} + p_{2i}\theta^2 + p_{4i}\theta^4$ for $i = 0$ and $i = 1$. The coefficients $p_{ji}$ are functions of the critical exponents $\beta$, $\delta$, and $\Delta$ and the constant $b^2$ as given in Table I.

The system-dependent constants that determine the scales of the fields $u_h$, $u_t$, and $u_1$ are represented by the coefficients $a$, $k_0$, and $k_1$. However, universality of the scaling functions implies that the constant $b^2$ be universal and we adopt the value

$$b^2 = 1.3757 \tag{18}$$

This value was originally determined from the experimental *PVT* data for steam [15] and it appears to reproduce the scaling function $f_0(x)$ within the accuracy to which this universal function is currently known theoretically [6, 13]. The corresponding universal values for the coefficients $p_{ji}$ are included in Table II in the Appendix, where the equations that specify the scaled fundamental equation are summarized.

## 4. APPLICATIONS

The scaled fundamental equation contains the following constants. First, the critical exponents $\beta$, $\delta$, and $\Delta$ and the scaling-function constant

$b^2$, which are universal and whose values are given by theory. In addition, the equation contains the following system-dependent constants: the critical-point parameters $T_c$, $P_c$, and $\rho_c$, the parameters $a$, $k_0$, $k_1$, and $c$, which determine the relationship between the scaling fields and the physical variables, the parameters $\tilde{P}_1$, $\tilde{P}_2$, $\tilde{P}_3$, and $\tilde{P}_{11}$, which determine the analytic background to the pressure, and the parameters $\tilde{\mu}_c$, $\tilde{\mu}_1$, $\tilde{\mu}_2$, and $\tilde{\mu}_3$, which determine the analytic background to the caloric properties, yielding a total of 15 parameters. Two of these parameters, namely $\tilde{\mu}_c$ and $\tilde{\mu}_1$, are related to the zero-point values of energy and entropy; in practice they are chosen so that the energy and entropy from the scaled equation become equal to those from available global thermodynamic equations away from the critical point.

We have determined the parameters for a number of fluids, with special emphasis on fluids that are important in engineering applications. The results thus far obtained are presented in Table III in the Appendix and include normal steam [15], heavy steam [18], ethylene [19], and isobutane [20]. Work on carbon dioxide is currently in progress. It turns out that the equation yields a correct physical representation of the experimental data in a density range of approximately 30% above and below the critical density $\rho_c$ at temperatures up to about 6% above $T_c$ and down to temperatures below $T_c$ where the vapor and liquid densities begin to differ by more than 30% from $\rho_c$. Detailed comparisons between the equation and the original experimental data for the various fluids are presented elsewhere [15, 18–20]. Here we restrict ourselves to some comments about the differences between the thermodynamic properties calculated from the universal scaled fundamental equation and those calculated from classical engineering equations that are analytic at the critical point.

As a representative example we consider heavy steam ($D_2O$). An analytic fundamental equation for $D_2O$ was recently formulated by Hill *et al.* [21, 22]; this equation has subsequently been adopted by the International Association for the Properties of Steam as the recommended formulation for the thermodynamic properties of fluid $D_2O$. The differences between the scaled fundamental equation and classical equations become most pronounced when considering properties like the compressibility or the specific heat which are related to derivatives of the thermodynamic surface. For instance, the scaled fundamental equation implies that the compressibility $K_T$ and the specific heat at constant pressure $C_p$ will asymptotically diverge as $|\Delta\tilde{T}|^{-\beta(\delta-1)} = |\Delta\tilde{T}|^{-1.24}$, while analytic equations can only accommodate an asymptotic divergence inversely proportional to $\Delta\tilde{T}$ [13]. In Fig. 1 we show a comparison between the experimental $C_p$ data of Rivkin and Egorov [23] for $D_2O$ in the critical region and our scaled fundamental equation. In Fig. 2 the same data are compared with the analytic equation of Hill *et al.* The scaled fundamental equation accommo-

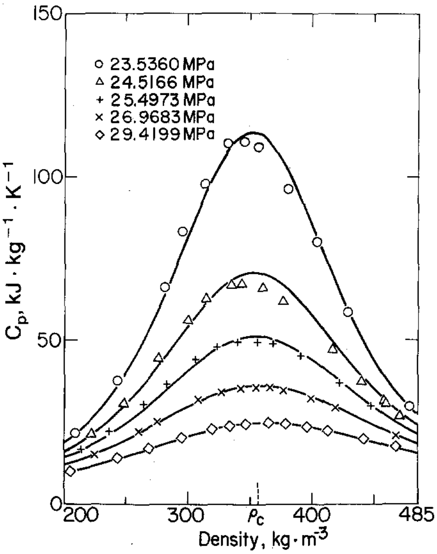

**Fig. 1.** The specific heat at constant pressure of $D_2O$ in the critical region at various pressures as a function of density. The data points are those of Rivkin and Egorov and the curves represent the values calculated from the universal scaled equation. (From [18].)

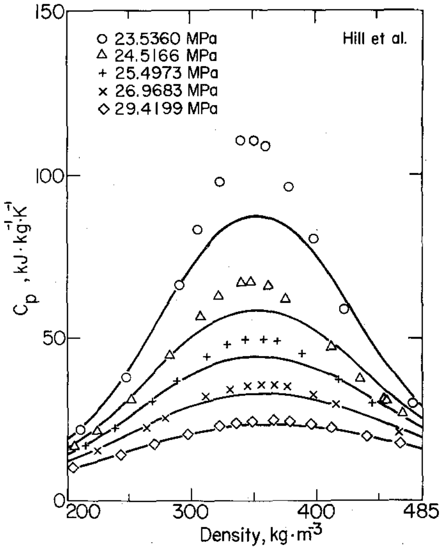

**Fig. 2.** The specific heat at constant pressure of $D_2O$ in the critical region at various pressures as a function of density. The data points are those of Rivkin and Egorov and the curves represent the values calculated from the analytic equation of Hill *et al.* (From [18].)

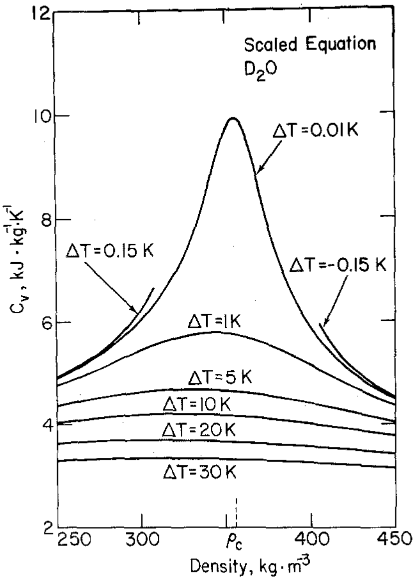

**Fig. 3.** The specific heat at constant volume of $D_2O$ as a function of density at various values $\Delta T = T - T_c$ as calculated from the universal scaled equation.

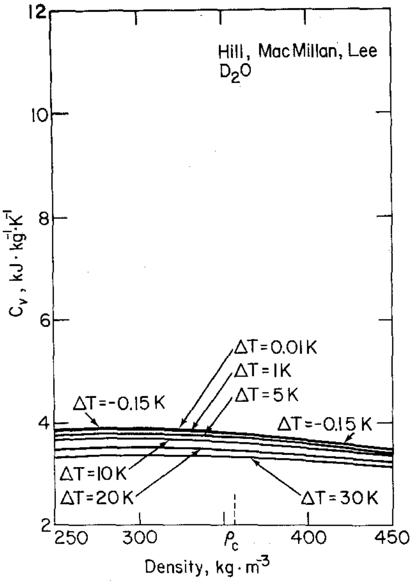

**Fig. 4.** The specific heat at constant volume of $D_2O$ as a function of density at various values of $\Delta T = T - T_c$ as calculated from the analytic equation of Hill *et al.*

dates the actual increase of the $C_p$ maxima as a function of temperature, but the analytic equation does not [18]. The differences between the scaled equation and the analytic equation are even more qualitative when one considers the specific heat at constant volume $C_v$. In Figs. 3 and 4 we have plotted $C_v$ as a function of density for various values of $\Delta T = T - T_c$ as calculated from the scaled equation and the analytic equation, respectively. The scaled equation implies that $C_v$ will diverge as $|\Delta \tilde{T}|^{\beta(\delta+1)-2} = |\Delta \tilde{T}|^{-0.1}$; in an analytic equation the specific heat must remain finite at the critical point [13]. The fact that the specific heat at constant volume diverges at the critical point has been well established experimentally [5, 24]. The analytic equation of Hill *et al.* does not account for such an increase of $C_v$ in the critical region. In the case of $D_2O$ we have only a few experimental $C_v$ data of unknown accuracy reported by Amirkhanov *et al.* [25]; these data do indicate a sharp increase near the critical point consistent with the predicted divergence as shown in Fig. 5.

Similar differences are obtained if our fundamental scaled equation is compared with the analytic equation of Keenan *et al.* [26] for ordinary steam, with the analytic equation of Jacobsen *et al.* [27] for ethylene, or with the analytic equation of Waxman and Gallagher [28] for isobutane. It should be noted that Waxman and Gallagher were well aware of the limitations of their analytic equation in the critical region and exclude from their surface the region around the critical point where large discrepancies appear [20, 28].

It is possible to improve the agreement between analytic equations and

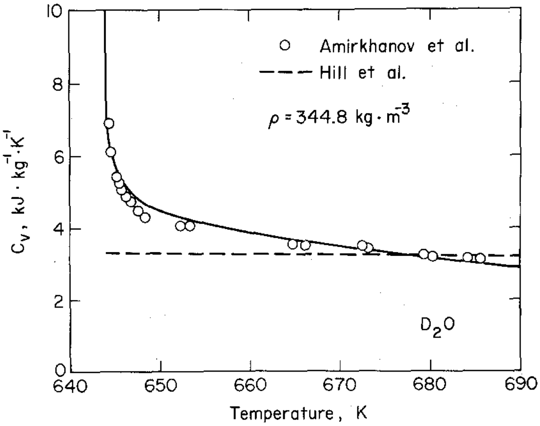

**Fig. 5.** The specific heat at constant volume of $D_2O$ in the one-phase region as a function of temperature at a density near the critical density. The data points are those of Amirkhanov *et al.* and the curves represent the values calculated from the universal scaled equation (—) and from the analytic equation of Hill *et al.* (- - -).

a finite set of experimental data by adding an adequate number of corrections terms. This procedure was adopted by Haar *et al.* [29] in formulating a new fundamental equation for fluid $H_2O$ adopted by the International Association for the Properties of Steam [30]. However, because of qualitatively unphysical features caused by these correction terms, a small region around the critical point has to be excluded from the equation [30, 31].

## 5. DISCUSSION

The renormalization-group theory of critical phenomena, originally introduced by Wilson and further developed by many researchers, does provide us with a new powerful method for a correct representation of the thermophysical properties of fluids in the critical region. Research to generalize the scaled fundamental equation so as to make it applicable in a larger range of temperatures and densities around the critical point is currently in progress [10, 32].

## APPENDIX. SCALED FUNDAMENTAL EQUATION

*Reduced thermodynamic quantities*:

$$\tilde{P} = \frac{P}{T}\frac{T_c}{P_c}, \qquad \tilde{T} = -\frac{T_c}{T}, \qquad \tilde{\mu} = \frac{\mu}{T}\frac{\rho_c T_c}{P_c}$$

*Fundamental equations*:

$$\Delta\tilde{T} = \tilde{T} + 1, \qquad \Delta\tilde{\mu} = \tilde{\mu} - \tilde{\mu}_c - \sum_{j=1}^{3} \tilde{\mu}_j (\Delta\tilde{T})^j$$

$$\tilde{P} = \Delta\tilde{P} + 1 + \Delta\tilde{\mu} + \tilde{P}_{11}\Delta\tilde{\mu}\Delta\tilde{T} + \sum_{j=1}^{3} \tilde{P}_j (\Delta\tilde{T})^j$$

**Table II.** Universal Critical-Region Constants

| | |
|---|---|
| $\beta$ | 0.325 |
| $\delta$ | 4.82 |
| $\Delta$ | 0.5 |
| $b^2$ | 1.3757 |
| $p_{00}$ | 0.586 535 |
| $p_{20}$ | − 1.026 243 |
| $p_{40}$ | 0.612 903 |
| $p_{01}$ | 0.103 25 |
| $p_{21}$ | 0.160 32 |
| $p_{41}$ | − 0.169 86 |

**Table III.** System-Dependent Critical-Region Constants

| | | Light steam [15] ($H_2O$) | Heavy steam [18] ($D_2O$) | Ethylene [19] | Isobutane [20] |
|---|---|---|---|---|---|
| Critical-point parameters | $T_c$ (K) | 647.067 | 643.89 | 282.3452 | 407.84 |
| | $P_c$ (MPa) | 22.0460 | 21.6713 | 5.0403 | 3.6290 |
| | $\rho_c$ ($kg \cdot m^{-3}$) | 322.778 | 356.238 | 214.165 | 225.5 |
| Scaling-field parameters | $a$ | 23.667 | 23.667 | 19.3214 | 22.0163 |
| | $k_0$ | 1.4403 | 1.4403 | 1.1229 | 1.1938 |
| | $k_1$ | 0.2942 | 0.2942 | 0.5462 | 0.5055 |
| | $c$ | $-0.01776$ | $-0.01776$ | $-0.00781$ | $-0.00968$ |
| Pressure background parameters | $\tilde{P}_1$ | 6.8445 | 6.9107 | 5.3350 | 5.8858 |
| | $\tilde{P}_2$ | $-25.4915$ | $-25.2370$ | $-18.1475$ | $-22.0805$ |
| | $\tilde{P}_3$ | 5.238 | 8.6180 | 0 | 0 |
| | $\tilde{P}_{11}$ | 0.4918 | 0.54764 | $-0.16669$ | $-0.06821$ |
| Caloric background parameters | $\tilde{\mu}_c$ | $-11.233$ | $-11.948$ | $-36.4889$ | $-4.9535$ |
| | $\tilde{\mu}_1$ | $-22.655$ | $-24.219$ | $-27.3955$ | $-21.6912$ |
| | $\tilde{\mu}_2$ | $-17.888$ | $-21.552$ | $-12.2091$ | $-32.2295$ |
| | $\tilde{\mu}_3$ | $-4.933$ | $+17.308$ | $-11.8802$ | $-33.5271$ |
| Range of validity | | $-0.005 \leqslant \Delta\tilde{T} \leqslant +0.066$<br>$0.62 \leqslant \tilde{\rho} \leqslant 1.30$ | $-0.009 \leqslant \Delta\tilde{T} \leqslant +0.057$<br>$0.62 \leqslant \tilde{\rho} \leqslant 1.30$ | $-0.012 \leqslant \Delta\tilde{T} \leqslant +0.059$<br>$0.75 \leqslant \tilde{\rho} \leqslant 1.38$ | $-0.007 \leqslant \Delta\tilde{T} \leqslant +0.069$<br>$0.70 \leqslant \tilde{\rho} \leqslant 1.35$ |

*Parametric representation*:

$$\Delta\tilde{\mu} = r^{\beta\delta} a\theta(1-\theta^2)$$

$$\Delta\tilde{T} = r(1 - b^2\theta^2) - c r^{\beta\delta} a\theta(1-\theta^2)$$

$$\Delta\tilde{P} = a r^{\beta(\delta+1)}\left[k_0 p_0(\theta) + r^{\Delta} k_1 p_1(\theta)\right]$$

with $p_i(\theta) = p_{0i} + p_{2i}\theta^2 + p_{4i}\theta^4$ $(i = 0, 1)$. The values of the constants in these equations are presented in Tables II and III. Explicit expressions for the various thermodynamic properties in terms of the constants of the scaled fundamental equation are given in Refs. 14 and 15.

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## REFERENCES

1. K. G. Wilson, *Rev. Mod. Phys.* **55**:583 (1983).
2. F. J. Wegner, *Phys. Rev. B* **5**:4529 (1972).
3. F. J. Wegner, in *Phase Transitions and Critical Phenomena*, Vol. 6. C. Domb and M. S. Green, eds. (Academic Press, New York, 1976), p. 7.
4. J. C. Le Guillou and J. Zinn-Justin, *Phys. Rev. B* **21**:3976 (1980).
5. S. C. Greer and M. R. Moldover, *Annu. Rev. Phys. Chem.* **32**:233 (1981).
6. J. V. Sengers, in *Phase Transitions: Cargèse 1980*, M. Levy, J. C. Le Guillou, and J. Zinn-Justin, eds. (Plenum Press, New York, 1982), p. 95.
7. H. Güttinger and D. S. Cannell, *Phys. Rev. A* **24**:3188 (1981).
8. M. W. Pestak and M. H. W. Chan, *Phys. Rev. B* **30** (in press).
9. J. F. Nicoll, *Phys. Rev. A* **24**:2203 (1981).
10. M. Ley-Koo and J. V. Sengers, in *Proceedings of the 8th Symposium on Thermophysical Properties*, J. V. Sengers, ed. (American Society of Mechanical Engineers, New York, 1982), Vol. I, p. 358.
11. M. Ley-Koo and M. S. Green, *Phys. Rev. A* **23**:2650 (1981).
12. M. E. Fisher, *Rep. Prog. Phys.* **30**(II):615 (1967).
13. J. V. Sengers and J. M. H. Levelt Sengers, in *Progress in Liquid Physics*, C. A. Croxton, ed. (Wiley, New York, 1978), p. 103.
14. J. M. H. Levelt Sengers and J. V. Sengers, in *Perspectives in Statistical Physics*, H. J. Raveché, ed. (North-Holland, Amsterdam, 1981), p. 240.
15. J. M. H. Levelt Sengers, B. Kamgar-Parsi, F. W. Balfour, and J. V. Sengers, *J. Phys. Chem. Ref. Data* **12**:1 (1983).
16. P. Schofield, J. D. Litster, and J. T. Ho, *Phys. Rev. Lett.* **23**:1090 (1969).
17. F. W. Balfour, J. V. Sengers, M. R. Moldover, and J. M. H. Levelt Sengers, in *Proceedings of the 7th Symposium on Thermophysical Properties*, A. Cezairliyan, ed. (American Society of Mechanical Engineers, New York, 1977), p. 786; *Phys. Lett.* **65A**:223 (1978).

18. B. Kamgar-Parsi, J. M. H. Levelt Sengers, and J. V. Sengers, *J. Phys. Chem. Ref. Data* **12**:513 (1983).
19. J. M. H. Levelt Sengers, G. A. Olchowy, B. Kamgar-Parsi, and J. V. Sengers, A Thermodynamic Surface for the Critical Region of Ethylene, NBS Technical Note 1189 (U.S. Gov't. Printing Office, Washington, D.C., 1984).
20. J. M. H. Levelt Sengers, B. Kamgar-Parsi, and J. V. Sengers, *J. Chem. Eng. Data* **28**:354 (1983).
21. P. G. Hill, R. D. C. MacMillan, and V. Lee, *J. Phys. Chem. Ref. Data* **11**:1 (1982); **13**: (1984).
22. P. G. Hill, R. D. MacMillan, and V. Lee, Tables of Thermodynamic Properties of Heavy Water in S.I. Units (Atomic Energy of Canada, Mississauga, Ontario, 1981).
23. S. L. Rivkin and B. N. Egorov, *Teploenergetika* **9**(5):62 (1962); *Atomnaya Energiya* **14**(6):581 (1963).
24. M. R. Moldover, in *Phase Transitions: Cargèse 1980*, M. Levy, J. C. Le Guillou, and J. Zinn-Justin, eds. (Plenum Press, 1982), p. 63.
25. Kh. I. Amirkhanov, G. B. Stepanov, B. A. Mussalov, and O. A. Bui, *Teploenergetika* **22**(4):68 (1973).
26. J. H. Keenan, F. G. Keyes, P. G. Hill, and J. G. Moore, *Steam Tables* (Wiley, New York, 1969).
27. R. T. Jacobsen, M. Jahangiri, R. B. Stewart, and R. I. Batchelor, A New Equation of State for Ethylene, Report No. 83-1 (Center for Applied Thermodynamic Studies, University of Idaho, 1983).
28. M. Waxman and J. S. Gallagher, *J. Chem. Eng. Data* **28**:224 (1983).
29. L. Haar, J. S. Gallagher, and G. S. Kell, in *Proceedings of the 8th Symposium on Thermophysical Properties*, J. V. Sengers, ed. (American Society of Mechanical Engineers, New York, 1982), Vol. II, p. 298.
30. The Provisional IAPS Formulation 1982 for the Thermodynamic Properties of Ordinary Water Substance for Scientific and General Use (Office of Standard Reference Data, National Bureau of Standards, Washington, D.C., 1984).
31. J. V. Sengers, J. T. R. Watson, R. S. Basu, B. Kamgar-Parsi, and R. C. Hendricks, *J. Phys. Chem. Ref. Data* (in press).
32. M. Ley-Koo, P. C. Albright, and J. V. Sengers, *Bull. Am. Phys. Soc.* **29**:681 (1984).