

## Global thermodynamic behavior of fluids in the critical region

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In a preceding publication [Z. Y. Chen, P. C. Albright, and J. V. Sengers, *Phys. Rev. A* **41**, 3161 (1990)] a procedure for constructing a thermodynamic free energy of fluids was proposed that incorporates crossover from singular behavior at the critical point to regular behavior far away from the critical point. In the present paper this procedure, based on an approximate solution of the renormalization-group theory of critical phenomena, is further extended so that it can be used in conjunction with a six-term classical Landau expansion. The resulting thermodynamic free energy yields a satisfactory representation of the thermodynamic properties of fluids in a large range of temperatures and densities around the critical point, as is demonstrated by a comparison with experimental thermodynamic-property data for carbon dioxide, steam, and ethane.

### I. INTRODUCTION

The nature of the singular behavior of the thermodynamic properties of fluids asymptotically close to the critical point is now well understood.<sup>1</sup> Specifically, this behavior can be characterized in terms of scaling laws with universal critical exponents and universal scaling functions.<sup>2</sup> The validity of the scaled equations, however, is restricted to a small range of temperatures and densities in the vicinity of the critical point.<sup>3</sup> On the other hand, critical effects on the thermodynamic properties of fluids are observed in practice in a large range of temperatures and densities around the critical point. Hence, to obtain a theoretically based global representation of the thermodynamic properties of fluids, we want to develop a thermodynamic free energy that not only incorporates the asymptotic critical behavior, but that also accounts for the crossover to the regular behavior far away from the critical point.

In a previous publication Chen, Albright, and Sengers (CAS) developed a procedure for transforming a classical Landau expansion for the thermodynamic free energy into a renormalized thermodynamic free energy that properly includes the effects of critical fluctuations. As an illustration CAS applied the procedure to a two-term Landau expansion.<sup>4</sup>

A crossover procedure on the basis of a two-term Landau expansion is by itself not adequate to obtain a global representation of the thermodynamic properties of fluids in the critical region. A two-term Landau expansion represents only the asymptotic limiting behavior of a classical equation. As such it suffers from two deficiencies: it not only fails in the critical region because it leads to wrong critical exponents, but it also fails in the classical region because two terms will not be enough. The work of CAS remedied the first deficiency but not the second one. In order to reproduce the actual classical

thermodynamic behavior far away from the critical point we shall need to consider a more complete classical equation. We shall therefore extend the crossover procedure so that it can be applied to a classical Landau expansion with an arbitrary number of terms. For this purpose we shall include an approximate treatment of the crossover behavior of the higher-order terms in temperature and density; specifically we shall include the crossover behavior associated with the confluent singularity due to terms asymmetric in the order parameter that are not present in the case of the symmetric Landau-Ginzburg-Wilson (LGW) model.<sup>5</sup> We shall then apply the procedure to a six-term classical Landau expansion and make a comparison with experimental thermodynamic-property data for carbon dioxide, steam, and ethane. This six-term Landau crossover model yields an accurate representation of the thermodynamic properties at almost all temperatures and densities where critical-fluctuation effects on the thermodynamic properties are observed.

The physical features of our crossover model have been discussed in a previous publication<sup>4</sup> and are not repeated here. However, in Sec. II we briefly review the two-term Landau crossover model with the purpose of introducing an improved representation of the solution of the flow equation associated with the renormalization-group theory of critical phenomena. In Sec. III we discuss the approximations adopted to construct a higher-order Landau crossover model. Some interesting features specific to fluids are then considered in Sec. IV. Comparisons with experimental data are presented in Sec. V.

### II. CROSSOVER MODEL

Let  $\rho$  be the density,  $T$  the temperature,  $P$  the pressure,  $\mu$  the chemical potential, and  $A/V$  the Helmholtz free energy per unit volume. These properties are made dimensionless<sup>1</sup> with the aid of the critical parameters  $\rho_c$ ,

$T_c$ , and  $P_c$ :

$$\begin{aligned} \bar{\rho} &= \frac{\rho}{\rho_c}, \quad \bar{T} = -\frac{T_c}{T}, \quad \bar{P} = \frac{PT_c}{P_c T}, \\ \bar{\mu} &= \frac{\mu\rho_c T_c}{P_c T}, \quad \bar{A} = \frac{AT_c}{VP_c T}. \end{aligned} \quad (2.1)$$

In addition we define

$$\Delta\bar{\rho} = \bar{\rho} - 1, \quad \Delta\bar{T} = \bar{T} + 1, \quad (2.2)$$

$$\Delta\bar{\mu} = \bar{\mu} - \bar{\mu}_0(\bar{T}), \quad (2.3)$$

$$\Delta\bar{A} = \bar{A} - \bar{\rho}\bar{\mu}_0(\bar{T}) - \bar{A}_0(\bar{T}), \quad (2.4)$$

where  $\bar{\mu}_0(\bar{T})$  and  $\bar{A}_0(\bar{T})$  are analytic (background) functions of  $\Delta\bar{T}$  subject to the conditions that at the critical temperature  $\Delta\bar{\mu} = 0$  and  $\bar{A}_0 = -1$ .

Classical equations of state are analytic functions of temperature and density near the critical point. Such equations are reduced to a mean-field theory, which implies that the critical part  $\Delta\bar{A}$  of the Helmholtz free-energy density has a Landau expansion of the form<sup>6</sup>

$$\Delta\bar{A}_{cl} = \frac{1}{2}tM^2 + \frac{u\Lambda}{4!}M^4 + \dots, \quad (2.5)$$

where the coefficient of the  $M^4$  term has been expressed<sup>5</sup> as a product of a coupling constant  $u$  and an ultraviolet cutoff parameter  $\Lambda$ . The temperaturelike variable  $t$  and the densitylike variable  $M$  in (2.5) are related to the actual physical variables  $\Delta\bar{T}$  and  $\Delta\bar{\rho}$  in a manner to be specified in Sec. IV. Asymptotically close to the critical point  $t$  and  $M$  become proportional to the temperature difference  $\Delta\bar{T}$  and the density difference  $\Delta\bar{\rho}$ , respectively. It is well known that the classical Landau expansion (2.5) does not yield a quantitative correct description of the actual asymptotic critical behavior of real systems.

According to the renormalization-group theory of critical phenomena, the singular part  $\Delta\bar{A}_s$  of the Helmholtz free-energy density satisfies a partial differential equation<sup>7-9</sup>

$$\begin{aligned} \left[ \Lambda \frac{\partial}{\partial \Lambda} + \beta(u) \frac{\partial}{\partial u} \right. \\ \left. + [2 - \nu^{-1}(u)]t \frac{\partial}{\partial t} - \frac{1}{2}\eta(u)M \frac{\partial}{\partial M} \right] \Delta\bar{A}_s \\ + \frac{1}{2}t^2\Lambda^{-1}B(u) = 0 \end{aligned} \quad (2.6)$$

where  $\beta(u)$ ,  $\nu(u)$ , and  $\eta(u)$  are renormalization functions to be specified below, while  $B(u)$  to a very good approximation can be taken to be unity.<sup>7,9</sup> From (2.6) it follows that  $\Delta\bar{A}_s(t, M, u, \Lambda)$  satisfies a rescaling relation of the form

$$\begin{aligned} \Delta\bar{A}_s(t, M, u, \Lambda) = \Delta\bar{A}_s[t\mathcal{T}(l), M\mathcal{D}^{1/2}(l), u(l), \Lambda(l)] \\ - \frac{1}{2}t^2\mathcal{H}(l), \end{aligned} \quad (2.7)$$

with

$$\Lambda(l) = \Lambda e^{-l}, \quad (2.8)$$

while  $u(l)$  satisfies the flow equation

$$\frac{du(l)}{dl} = -\beta(u(l)), \quad (2.9)$$

with the boundary condition

$$u(l=0) = u. \quad (2.10)$$

For  $l \rightarrow \infty$ ,  $u(l)$  approaches a fixed point  $u^*$  such that

$$\beta(u^*) = 0. \quad (2.11)$$

The rescaling functions  $\mathcal{T}(l)$ ,  $\mathcal{D}(l)$ , and  $\mathcal{H}(l)$  in (2.7) are given by

$$\mathcal{T}(l) = \exp \left[ - \int_0^l [2 - \nu^{-1}(u(s))] ds \right], \quad (2.12)$$

$$\mathcal{D}(l) = \exp \left[ \int_0^l \eta(u(s)) ds \right], \quad (2.13)$$

$$\begin{aligned} \mathcal{H}(l) &= \Lambda^{-1} \int_0^l B(u(s)) \mathcal{T}^2(s) e^s ds \\ &\simeq \Lambda^{-1} \int_0^l \mathcal{T}^2(s) e^s ds. \end{aligned} \quad (2.14)$$

Based on earlier work of Nicoll and co-workers,<sup>9,10</sup> CAS showed that the mean-field expression (2.5) for the critical part of the Helmholtz free-energy density can be transformed into a renormalized critical part  $\Delta\bar{A}_r$  as

$$\begin{aligned} \Delta\bar{A}_r(t, M; u, \Lambda) &= \frac{1}{2}t\mathcal{T}(l^*)M^2\mathcal{D}(l^*) \\ &+ \frac{u\Lambda\mathcal{U}(l^*)}{4!}M^4\mathcal{D}^2(l^*) - \frac{1}{2}t^2\mathcal{H}(l^*), \end{aligned} \quad (2.15)$$

where  $l = l^*$  is a match-point value such that

$$\Lambda e^{-l^*} = \kappa(l^*), \quad (2.16)$$

with

$$\kappa^2 = t\mathcal{T}(l^*) + \frac{1}{2}u\Lambda\mathcal{U}(l^*)M^2\mathcal{D}(l^*), \quad (2.17)$$

and where the function  $\mathcal{U}(l)$  is defined by

$$u\Lambda\mathcal{U}(l) = u(l)\Lambda(l). \quad (2.18)$$

To implement this procedure we need explicit expressions for the renormalization functions  $\beta(u)$ ,  $\nu(u)$ , and  $\eta(u)$ . These renormalization functions satisfy the conditions

$$\beta(0) = \beta(u^*) = 0, \quad (2.19)$$

$$\beta'(0) = -1, \quad (2.20)$$

$$\beta'(u^*) = \omega = \Delta/\nu, \quad (2.21)$$

$$\nu(u^*) = \nu, \quad (2.22)$$

$$\eta(u^*) = \eta, \quad (2.23)$$

with  $\beta'(u) = d\beta(u)/du$ . Here  $\nu = 0.63$  and  $\eta = 0.033$  are the critical exponents that characterize the asymptotic behavior of the correlation function, while  $\omega \simeq 0.81$  or  $\Delta \simeq 0.51$  are exponents associated with the first Wegner correction-to-scaling term.<sup>11-13</sup> As an approximant for  $\beta(u)$  that satisfies (2.19)–(2.21) we adopt an expression

proposed by Schloms and Dohm<sup>14</sup>

$$\beta(\bar{u}) = -\frac{\omega u^* \bar{u}(1-\bar{u})}{\omega + (1-\omega)\bar{u}}, \quad (2.24)$$

with

$$\bar{u} = u/u^*. \quad (2.25)$$

This expression is an improvement over the expression  $\beta(\bar{u}) = -\omega u^* \bar{u}(1-\bar{u})$  adopted earlier by CAS. Expression (2.24) is consistent with perturbation theory up to order  $u^3$  if an expansion in  $u$  is made, and it gives a very good approximation of the numerical Borel resummation of  $\beta(\bar{u})$  for all values of  $\bar{u}$  if the actual values of  $\omega$  and  $u^*$  are used.<sup>14</sup> For the functions  $\nu(u)$  and  $\eta(u)$  we continue to use<sup>4,15</sup>

$$2-\nu^{-1}(\bar{u}) = (2-\nu^{-1})\bar{u}, \quad (2.26)$$

$$\eta(\bar{u}) = \eta\bar{u}^2. \quad (2.27)$$

Although (2.26) and (2.27) are only accurate to leading order in  $u$ , it can be shown that they are very good approximations for  $\nu(\bar{u})$  and  $\eta(\bar{u})$  in practice, if actual values of the critical exponents are used. These expressions are also identical to approximants proposed by Schloms and Dohm.<sup>14</sup>

We find it convenient to define

$$Y(l) = \frac{u(l) - u^*}{u - u^*}. \quad (2.28)$$

When (2.24) is substituted into (2.9) the flow equation can be integrated analytically with the result

$$1 - (1 - \bar{u})Y(l) = \bar{u}e^l Y^{1/\omega}(l). \quad (2.29)$$

The function  $Y \equiv Y(l^*)$ , to be designated as the ‘‘crossover’’ function, has to be evaluated at the matching-point value  $l = l^*$  determined by (2.16), so that

$$1 - (1 - \bar{u})Y(l^*) = \bar{u} \frac{\Lambda}{\kappa} Y^{1/\omega}(l^*). \quad (2.30)$$

However, as argued by CAS, to recover the correct classical behavior away from the critical point the parameter  $\Lambda/\kappa$  in (2.30) should be replaced by  $[1 + (\Lambda/\kappa)^2]^{1/2}$ . In practice, we therefore evaluate the crossover function  $Y$  from

$$1 - (1 - \bar{u})Y = \bar{u}[1 + (\Lambda/\kappa)^2]^{1/2} Y^{1/\omega}. \quad (2.31)$$

The substitution of (2.28) into (2.12)–(2.14) and (2.18) yields

$$\begin{aligned} \mathcal{T}(l) &= Y^{(2-\nu^{-1})/\omega}(l) \\ &\quad \times \exp\{- (2-\nu^{-1})(1-\omega^{-1})[\bar{u}(l) - \bar{u}]\}, \end{aligned} \quad (2.32)$$

$$\begin{aligned} \mathcal{D}(l) &= Y^{-\eta/\omega}(l) \exp\{\eta\left[\frac{1}{2}(1-\omega^{-1})[\bar{u}(l) + \bar{u}] - \omega^{-1}\right] \\ &\quad \times [\bar{u}(l) - \bar{u}]\}, \end{aligned} \quad (2.33)$$

$$\begin{aligned} \mathcal{H}(l) &= \frac{\nu}{\alpha\bar{u}\Lambda} [Y^{-\alpha/\nu\omega}(l) - 1] \\ &\quad + \frac{\omega - 1}{\bar{u}\Lambda(\omega - \alpha/\nu)} (\bar{u} - 1) [Y^{1-\alpha/\nu\omega}(l) - 1], \end{aligned} \quad (2.34)$$

$$\mathcal{U}(l) = Y^{1/\omega}(l), \quad (2.35)$$

where  $\alpha = 2 - 3\nu = 0.11$  is the critical exponent of the asymptotic power-law behavior of the specific heat.<sup>1</sup> These rescaling functions need to be evaluated for  $l = l^*$ . In practice we take for the rescaling functions  $\mathcal{T} \equiv \mathcal{T}(l^*)$ ,  $\mathcal{D} \equiv \mathcal{D}(l^*)$ ,  $\mathcal{H} \equiv \mathcal{H}(l^*)$ , and  $\mathcal{U} \equiv \mathcal{U}(l^*)$  the approximate expressions (we drop the explicit notation  $l = l^*$  in the remainder of this paper)

$$\mathcal{T} = Y^{(2-\nu^{-1})/\omega}, \quad (2.36)$$

$$\mathcal{D} = Y^{-\eta/\omega}, \quad (2.37)$$

$$\mathcal{H} = \frac{\nu}{\alpha\bar{u}\Lambda} (Y^{-\alpha/\nu\omega} - 1), \quad (2.38)$$

$$\mathcal{U} = Y^{1/\omega}, \quad (2.39)$$

to be substituted into (2.15). The crossover function  $Y$  is evaluated from (2.31) with  $\kappa$  given by (2.17)

$$\kappa^2 = t\mathcal{T} + \frac{1}{2}u\Lambda\mathcal{U}M^2\mathcal{D}. \quad (2.40)$$

In the limit  $\Lambda/\kappa \rightarrow \infty$  or  $Y \rightarrow 0$  we recover the asymptotic scaled critical behavior, and in the limit  $\Lambda/\kappa \rightarrow 0$  or  $Y \rightarrow 1$  we recover the classical Landau expression.<sup>4</sup>

The expression (2.39) for  $\mathcal{U}$  is identical to (2.35), but the expressions (2.36)–(2.38) for the rescaling functions  $\mathcal{T}$ ,  $\mathcal{D}$ , and  $\mathcal{H}$  are simplified versions of the solutions given by (2.32)–(2.34). The effect of these approximations can be investigated by considering the universal ratios of the amplitudes in the Wegner expansion around the critical point.<sup>1</sup> Let  $A^+$  and  $A^-$  be the amplitudes of the asymptotic power laws for the isochoric specific heat above and below  $T_c$ ,  $\Gamma^+$  and  $\Gamma^-$  the amplitudes of the asymptotic power laws for the susceptibility  $\chi = (\partial\bar{\rho}/\partial\bar{\mu})_T$  above and below  $T_c$ , and  $B$  the amplitude of the asymptotic power law for the order parameter along the coexistence boundary. Similarly, let  $A_1^+$ ,  $\Gamma_1^+$ , and  $B_1$  be the amplitude of the first Wegner correction term in the expansion of these properties.<sup>1,4</sup> In Table I we compare the values predicted theoretically for the amplitude ratios  $A^+/A^-$ ,  $\Gamma^+/\Gamma^-$ ,  $A^+\Gamma^+/B^2$ ,  $A_1^+/\Gamma_1^+$ , and  $B_1/\Gamma_1^+$  with the values implied by our crossover model. It is seen that the approximations implied by Eqs. (2.36)–(2.38) affect the amplitudes of the Wegner correction terms; the value for  $B_1/\Gamma_1^+$  becomes even better, while the value for  $A_1^+/\Gamma_1^+$  becomes slightly worse.

We note that the crossover function  $Y$  is evaluated from (2.29), while CAS evaluated this crossover function from<sup>4</sup>

$$Y_{\text{CAS}} = \{1 + \bar{u}[(1 + \Lambda^2/\kappa^2)^{\omega/2} - 1]\}^{-1}. \quad (2.41)$$

The rescaling functions  $\mathcal{H}$  and  $\mathcal{U}$ , given by (2.38) and (2.39), also differ from the expression used by CAS. These differences are due to the adoption of the theoretically more satisfactory representation (2.24) for  $\beta(u)$ , which satisfies  $\beta'(0) = -1$ , while the approximant of CAS implies  $\beta'(0) = -\omega$ . Furthermore, we found it convenient to remove any explicit dependence on  $\bar{u}$  in the definition of  $\mathcal{U}$ . Close to the critical point, (2.41) reduces to  $Y_{\text{CAS}} \simeq \kappa^\omega/\bar{u}\Lambda^\omega$ , while (2.31) implies

$$Y = \kappa^\omega/\bar{u}^\omega\Lambda^\omega \quad \text{for } \kappa \rightarrow 0. \quad (2.42)$$

TABLE I. Critical-amplitude ratios.

	Asymptotic amplitudes			Correction-to-scaling amplitudes		
	$A^+ / A^-$	$\Gamma^+ / \Gamma^-$	$A^+ \Gamma^+ / B^2$	$\Gamma^+ D B^{\delta-1}$	$A_1^+ / \Gamma_1^+$	$B_1 / \Gamma_1^+$
With Eqs. (2.32)–(2.35)	0.50	5.0	0.052	1.72	0.94	0.59
With Eqs. (2.36)–(2.39)	0.50	5.0	0.052	1.72	0.72	0.87
From theory	$0.52 \pm 0.01^{a,b}$	$4.95 \pm 0.15^b$	$0.058 \pm 0.001^b$	$1.67^c$	$0.9 \pm 0.1^{b,c}$	$0.9 \pm 0.2^d$

<sup>a</sup>References 16 and 18.

<sup>b</sup>Reference 13.

<sup>c</sup>Reference 9.

<sup>d</sup>Reference 18.

<sup>e</sup>Reference 17.

Hence the values found for  $\bar{u}$  and  $\Lambda$  in this paper will differ from those found by CAS, since the product  $\bar{u}\Lambda^\omega$  has been changed into  $\bar{u}^\omega\Lambda^\omega$ . However, we find that these modifications have negligibly small effects on the comparison with actual experimental data.

### III. EXTENSION TO A SIX-TERM LANDAU EXPANSION

As mentioned earlier, applying the crossover procedure to a classical Landau expansion truncated after two terms is by itself not sufficient to obtain a global representation of the thermodynamic properties in the critical region. As a next approximation we therefore consider

$$\Delta \tilde{A}_{cl} = \frac{1}{2}tM^2 + \frac{u\Lambda}{4!}M^4 + \frac{a_{05}}{5!}M^5 + \frac{a_{06}}{6!}M^6 + \frac{a_{14}}{4!}tM^4 + \frac{a_{22}}{2!2!}t^2M^2 + \dots, \quad (3.1)$$

keeping in mind that in the mean-field approximation  $M^2$  is of order  $t$ .

An important difference between (3.1) and (2.5) is the appearance of a term proportional to  $M^5$  which is a term odd in the order parameter  $M$ . Its crossover behavior is related to the appearance of odd terms in the LGW model and they are known to result in a new confluent singularity<sup>5,19,20</sup> with an exponent  $\omega_a = 2.1 \pm 0.2$ . The crossover behavior of the leading asymmetric terms has been analyzed by Nicoll and co-workers.<sup>5,21</sup> The main effects of their analysis can be summarized as follows. The  $M^5$  term in (3.1) is to be replaced by  $M^5 \mathcal{D}^{5/2} \mathcal{V} \mathcal{U}$  with

$$\mathcal{V} = Y^{(2\omega_a - 1)/2\omega}. \quad (3.2)$$

The asymmetric terms in the LGW model also lead to additive nonscaling contributions to the free energy like the last term in (2.15); for simplicity we neglect the asymmetric nonscaling terms here. In principle, there are other asymmetric terms like  $tM^3$  present in the expansion (3.1). However, the effects of such terms can be incorporated by introducing mixing of variables and a global asymmetry in the relationship between the theoretical variables  $t$  and  $M$  and the physical variables  $\Delta \tilde{T}$  and  $\Delta \tilde{p}$  as discussed in Sec. IV. Hence they do not need to be in-

cluded explicitly in the expansion (3.1).

Higher-order terms in the LGW model produce higher-order confluent singularities characterized by new correction-to-scaling exponents.<sup>19</sup> For example, the next singularity is characterized by the exponent  $\Delta_2 \simeq 1$ , which is less important than the leading confluent singularity with  $\Delta = 0.5$ . Moreover, Kayser and Raveché have argued that the long-range van der Waals forces between molecules yield additional confluent singularities not accounted for by a LGW model although their amplitudes are expected to be small.<sup>22</sup> All these singularities crossover to analytic terms in the classical limit. The exact crossover behavior of these higher-order terms is expected to be unimportant. Instead of considering the crossover behavior of these terms one by one, we assume that the crossover behavior of all higher-order terms can be treated approximately by replacing the variables  $t$  and  $M$  in all terms with the leading crossover functions only. Hence the actual crossover Helmholtz free-energy density  $\Delta \tilde{A}_r$  is constructed from the classical free energy  $\Delta \tilde{A}_{cl}(t, M)$  by the following transformation: (i) replace the variable  $t$  with  $t \mathcal{T} \mathcal{U}^{-1/2}$ ; (ii) replace the variable  $M$  in the even terms with  $M \mathcal{D}^{1/2} \mathcal{U}^{1/4}$ ; (iii) replace the variable  $M$  in the odd terms with  $M \mathcal{D}^{1/2} \mathcal{V}^{1/5} \mathcal{U}^{1/5}$ ; (iv) add a nonscaling fluctuation contribution of the form  $-\frac{1}{2}t^2 \mathcal{H}$ , while the distance variable  $\kappa$  is represented by (2.40).

One may notice that in this transformation the temperaturelike field  $t$  is replaced by  $t \mathcal{T} \mathcal{U}^{-1/2}$  rather than by  $t \mathcal{T}$  as in (2.7). In this section we have adopted the convention that the coefficient  $u\Lambda$  in (3.1) does not need to be replaced by any crossover counterpart as done in (2.15) as earlier by CAS; the additional  $\mathcal{U}^{-1/2}$  factor reproduces the same result.

We note that application of this crossover transformation is not restricted to an explicit Landau expansion for  $\Delta \tilde{A}_{cl}$  but can also be used in conjunction with any classical equation for  $\Delta \tilde{A}_{cl}$ , as, e.g., was done by Albright *et al.* for the van der Waals equation.<sup>23</sup> However, care should be taken that the classical equation be a “bare” classical equation that does not include effective analytic terms to approximate fluctuation contributions.

When the crossover transformation is applied to the Landau expansion (3.1) truncated after six-terms we obtain

$$\begin{aligned} \Delta \tilde{A}_r = & \frac{1}{2} t M^2 \mathcal{T} \mathcal{D} + \frac{1}{4!} u \Lambda M^4 \mathcal{D}^2 \mathcal{U} + \frac{1}{5!} a_{05} M^5 \mathcal{D}^{5/2} \mathcal{V} \mathcal{U} \\ & + \frac{1}{6!} a_{06} M^6 \mathcal{D}^3 \mathcal{U}^{3/2} + \frac{1}{4!} a_{14} t M^4 \mathcal{T} \mathcal{D}^2 \mathcal{U}^{1/2} \\ & + \frac{1}{2!} a_{22} t^2 M^2 \mathcal{T}^2 \mathcal{D} \mathcal{U}^{-1/2} - \frac{1}{2} t^2 \mathcal{H}, \end{aligned} \quad (3.3)$$

with the functions  $\mathcal{T}$ ,  $\mathcal{D}$ ,  $\mathcal{U}$ ,  $\mathcal{V}$ , and  $\mathcal{H}$  given by (2.36)–(2.39) and (3.2) in terms of the crossover function  $Y$  to be determined from (2.31) as a function of the distance parameter  $\kappa$  defined by (2.40).

#### IV. APPLICATION TO FLUIDS

As discussed by CAS, the crossover Helmholtz free-energy density derived on the basis of the LGW model for critical fluctuations can be applied to fluids through the identification<sup>4</sup>

$$M = c_\rho (\Delta \bar{\rho} - d_1 \Delta \tilde{T}) + c \left[ \frac{\partial \Delta \tilde{A}_r}{\partial t} \right]_M, \quad (4.1a)$$

$$t = c_t \Delta \tilde{T} + c \left[ \frac{\partial \Delta \tilde{A}_r}{\partial M} \right]_t, \quad (4.1b)$$

with the corresponding transformation

$$\Delta \tilde{A} = \Delta \tilde{A}_r - c \left[ \frac{\partial \Delta \tilde{A}_r}{\partial M} \right]_t \left[ \frac{\partial \Delta \tilde{A}_r}{\partial t} \right]_M. \quad (4.1c)$$

Here  $c_\rho$ ,  $c_t$ ,  $c$ , and  $d_1$  are system-dependent constants;  $c_\rho$  and  $c_t$  relate the scale of the physical variables  $\Delta \bar{\rho}$  and  $\Delta \tilde{T}$  to the theoretical variables  $M$  and  $t$ , while the coefficients  $c$  and  $d_1$  arise because of vapor-liquid asymmetry. As discussed by CAS, upon expanding (3.3) for  $\kappa \rightarrow 0$  one recovers the asymptotic critical power laws as well as the first Wegner correction terms. Furthermore, the crossover function (3.2) to be substituted into the  $M^5$  term also ensures that the leading asymmetric confluent singularity is reproduced. For instance, the renormalization-group theory of critical phenomena predicts that the diameter  $(\rho_l + \rho_v)/2\rho_c$  of the coexisting vapor and liquid densities has an expansion of the form<sup>19</sup>

$$\begin{aligned} (\rho_l + \rho_v)/2\rho_c = & 1 + d_{s1} |\Delta \tilde{T}|^{1-\alpha} + d_1 \Delta \tilde{T} \\ & + d_{s2} |\Delta \tilde{T}|^{1-\alpha+\Delta} + d_{a1} |\Delta \tilde{T}|^{\beta+\Delta_a} + \dots, \end{aligned} \quad (4.2)$$

with  $\Delta_a = \nu\omega_a$ . It can be readily verified that all these terms are recovered from our crossover Helmholtz free-energy density, the coefficients  $d_{s1}$ ,  $d_{s2}$ , and  $d_{a1}$  being functions of  $\bar{u}$ ,  $\Lambda$ , and the coefficients in the transformation (4.1). The coefficient  $d_1$  represents the slope of a linear temperature dependence of the coexistence-curve diameter close to the critical temperature. Farther away from the critical temperature other asymmetric terms also contribute to the linear temperature dependence of the coexistence-curve diameter so that the coefficient  $d_1$  in (4.2) cannot be identified with the slope of the diameter far away from the critical point.<sup>3,4,24</sup> We note that in the previous paper CAS defined the combination

$\bar{\rho} - 1 - d_1 \Delta \tilde{T}$  appearing in (4.1a) as  $\Delta \bar{\rho}$ . Here we use the more conventional definition<sup>1</sup>  $\Delta \bar{\rho} = \bar{\rho} - 1$  in accordance with (2.2).

In applying the crossover model to fluids we continue to use for the critical exponents and the fixed-point value of  $u^*$  the values adopted by CAS and listed in Table II. These values are in good agreement with the theoretically predicted universal values for three-dimensional Ising-like critical systems.<sup>11–13</sup>

The total Helmholtz free-energy density is related to  $\Delta \tilde{A}$  in accordance with (2.4),

$$\tilde{A} = \bar{\rho} \bar{\mu}_0(\tilde{T}) + \tilde{A}_0(\tilde{T}) + \Delta \tilde{A}. \quad (4.3)$$

The background functions  $\bar{\mu}_0(\tilde{T})$  and  $\tilde{A}_0(\tilde{T})$  are analytic functions of the temperature which in principle should be obtained from a classical equation. Since the precise functional form of these background functions are not important ingredients of our crossover model, we represent  $\bar{\mu}_0(\tilde{T})$  and  $\tilde{A}_0(\tilde{T})$  by truncated Taylor expansions to specify the Helmholtz free-energy density completely:

$$\bar{\mu}_0(\tilde{T}) = \sum_{j=0} \bar{\mu}_j (\Delta \tilde{T})^j, \quad (4.4)$$

$$\tilde{A}_0(\tilde{T}) = -1 + \sum_{j=1} \tilde{A}_j (\Delta \tilde{T})^j. \quad (4.5)$$

Our crossover Helmholtz free-energy density contains a number of system-dependent constants. First, the critical parameters  $T_c$ ,  $\rho_c$ , and  $P_c$  are needed; they are determined from an analysis of experimental data very close to the critical point. Second, the crossover model contains the crossover parameters  $\bar{u}$  and  $\Lambda$ . The parameter  $1 - \bar{u}$  is a measure of the importance of the leading Wegner corrections to scaling.<sup>4</sup> The parameter  $\Lambda$  is a measure of the wave number for which the fluctuations become microscopic; it can be related to an actual dimensional cutoff wave number  $q_D$  as

$$\Lambda = c_q q_D, \quad (4.6)$$

where  $c_q$  is the scale factor in the relationship  $\kappa = c_q \xi^{\epsilon-1}$  between  $\kappa$  and the inverse correlation length  $\xi$ . For  $\kappa \ll 1$  at  $M=0$ ,  $\kappa^2 \simeq t Y^{(2-\nu^{-1})/\omega}$ , while  $Y \simeq \kappa^\omega / \bar{u}^\omega \Lambda^\omega$  in accordance with (2.42), so that  $\kappa = (\bar{u} \Lambda)^{-(2\nu-1)} t^\nu$ . Since the correlation length  $\xi$  diverges as  $\xi = \xi^+ (\Delta \tilde{T})^{-\nu}$  and since  $t = c_t \Delta \tilde{T}$  asymptotically, the coefficient  $c_q$  may be estimated as<sup>4</sup>

$$c_q = c_t^\nu (\bar{u} \Lambda)^{-(2\nu-1)} \xi^+. \quad (4.7)$$

The crossover parameters  $\bar{u}$  and  $\Lambda$ ; the scaling-field parameters  $c_\rho$ ,  $c_t$ ,  $c$ , and  $d_1$ ; the coefficients  $a_{05}$ ,  $a_{06}$ ,  $a_{14}$ ,

TABLE II. Universal critical-region constants.

$\nu = 0.630$
$\eta = 0.0333$
$\alpha = 2 - 3\nu = 0.110$
$\Delta = 0.51$ ( $\omega = \Delta/\nu = 0.80952$ )
$\omega_a = 2.1$
$u^* = 0.472$

and  $a_{22}$  of the Landau expansion; and the background parameter  $\bar{A}_j$  are determined by fitting the crossover model to experimental  $P$ - $\rho$ - $T$  data. In addition, the caloric background parameters  $\bar{\mu}_j$  ( $j \geq 2$ ) are determined from a comparison with caloric properties such as specific heat or velocity of sound;<sup>4</sup> the parameters  $\bar{\mu}_0$  and  $\bar{\mu}_1$  are related to the zero-point values of energy and entropy. The equation specifying the various thermodynamic properties are presented in Appendixes A and B. The numerical calculations proceed in the same way as described by CAS for the two-term Landau crossover model.<sup>4</sup>

## V. COMPARISON WITH EXPERIMENTAL DATA

### A. Carbon dioxide

As a first example we consider carbon dioxide, which was earlier considered by CAS in applying the two-term Landau crossover model.<sup>4,25</sup> The primary source of experimental  $P$ - $\rho$ - $T$  data for carbon dioxide is the measurements of Michels and co-workers,<sup>26–28</sup> while Edwards and Buckingham more recently obtained accurate specific-heat data for carbon dioxide in the critical region.<sup>29,30</sup>

An experimental determination of the critical parameters of carbon dioxide has been reported by Moldover,<sup>31</sup> for the critical temperature a value  $T_c = 304.127$  K was found. The subsequent specific-heat data of Edwards and Buckingham<sup>29</sup> appeared to imply  $T_c = 304.107$  K and this was the value adopted by Albright *et al.* in their previous analyses of the thermodynamic properties of carbon dioxide in the critical region.<sup>4,25,30</sup> Subsequently, the critical temperature of carbon dioxide was redetermined by Morrison,<sup>32</sup> who obtained  $T_c = 304.132$  K, a value close to the earlier one found by Moldover. For the purpose of the present paper, therefore, we fixed the critical parameters of carbon dioxide at the values proposed by Moldover.<sup>31</sup>

As mentioned in Sec. IV, the crossover parameters  $\bar{u}$  and  $\bar{\Lambda}$ ; the scaling-field parameters  $c_\rho$ ,  $c_t$ ,  $c$ , and  $d_1$ ; the coefficients  $a_{05}$ ,  $a_{06}$ ,  $a_{14}$ , and  $a_{22}$  of the classical expansion; and the background parameters  $\bar{A}_j$  were all determined from a fit to the experimental  $P$ - $\rho$ - $T$  data.<sup>26–28</sup> In the comparison with the experimental  $P$ - $\rho$ - $T$  data a correction has been applied for the differences between the temperatures  $T_M$  reported by Michels *et al.* and the temperatures  $T_{68}$  on the International Practical Temperature Scale<sup>33</sup> as shown in Table III. For temperatures below  $T_c$  these differences were earlier determined by Levelt Sengers and Chen<sup>34</sup> from a comparison of their experimental vapor pressures with those of Michels, Blaisse, and Michels.<sup>28</sup> For temperatures above  $T_c$  we extended their procedure by comparing the experimental pressures obtained by Levelt Sengers and Chen with those obtained by Michels *et al.* along the critical isochore. This procedure requires the additional assumption that the CO<sub>2</sub> sample of Levelt Sengers and Chen had indeed the actual critical density, enabling us to extend the comparison to 40°C. At temperatures above 40°C we simply applied the same correction as at 40°C. The caloric background parameters were determined from a

TABLE III. Apparent differences between the temperatures  $T_{68}$  on the International Practical Temperature Scale and the temperatures  $T_M$  reported by Michels *et al.*

$T_M$ (°C)	$T_M - T_{68}$ (°C)
2.853	0.071
10.822	0.073
19.874	0.075
25.070	0.093
25.298	0.093
28.052	0.044
29.929	0.038
30.409	0.041
31.013	0.031
31.185	0.031
31.320	0.034
31.523	0.039
32.054	0.036
34.721	0.029
40.087	0.021

comparison with the isochore specific-heat data of Edwards and Buckingham,<sup>29</sup> supplemented with specific-heat values reported by Michels and de Groot for temperatures and densities farther away from the critical point.<sup>35</sup> In the comparison with the  $C_v$  data of Edwards and Buckingham a temperature correction of 0.02 K was applied to account for the apparent shift in  $T_c$  mentioned above. In addition, a revised estimate for the heat capacity of the empty calorimeter was included as determined by Albright *et al.*<sup>30</sup> The values of the various system-dependent parameters obtained are presented in Table IV.

The range of validity of the six-term Landau crossover model, when applied to carbon dioxide, is shown in Fig. 1. This range of validity corresponds to

$$\bar{\chi}^{-1} \leq 2.38. \quad (5.1)$$

This condition corresponds to a temperature range

$$291 \text{ K} \leq T \leq 373 \text{ K} \quad \text{at } \rho = \rho_c \quad (5.1a)$$

and a density range

$$193 \text{ kg/m}^3 \leq \rho \leq 712 \text{ kg/m}^3 \quad \text{at } T = T_c. \quad (5.1b)$$

When only two terms in the classical Landau expansion are retained, as was done by CAS,<sup>4</sup> the range indicated by (5.1) reduces to  $\bar{\chi}^{-1} \leq 0.6$ ; this range is also shown in Fig. 1. We note that CAS specified the range of validity in terms of the distance function  $\bar{R} \equiv (\partial^2 \Delta \bar{A} / \partial M^2)_t$ , which is related to the inverse susceptibility  $\bar{\chi}^{-1} \equiv (\partial^2 \Delta \bar{A} / \partial \Delta \rho^2)_{\Delta T}$  by  $\bar{\chi}^{-1} = c_\rho^2 \bar{R} G^{-1}$  with the function  $G$  specified by Eq. (B17) of Appendix B.

A comparison between the experimental pressures of Michels *et al.*<sup>26–28</sup> and the pressures calculated from the six-term Landau crossover model is shown in Fig. 2. With  $\sigma_\rho = 0.0001$  MPa,  $\sigma_T = 0.005$  K, and  $\sigma_\rho = 0.01\%$  as the estimated errors in pressure, temperature, and densi-

TABLE IV. System-dependent constants in six-term Landau crossover model.

		Carbon dioxide	Steam	Ethane
Critical-point parameters	$T_c$	304.127 K	647.067 K	305.33 K
	$P_c$	7.3753 MPa	22.046 MPa	4.8718 MPa
	$\rho_c$	467.83 kg/m <sup>3</sup>	322.788 kg/m <sup>3</sup>	206.6 kg/m <sup>3</sup>
Crossover parameters	$\bar{u}$	0.398 03	0.497 30	0.3691
	$\Lambda$	1.4214	1.4145	1.1216
Scaling-field parameters	$c_t$	1.9551	2.3712	1.5558
	$c_\rho$	2.4145	2.0845	2.4995
	$c$	-0.025 90	-0.092 831	-0.028 92
Classical parameters	$a_{05}$	-0.270 63	-0.357 16	-0.055 078
	$a_{06}$	1.142 28	1.948 28	0.977 78
	$a_{14}$	0.398 39	0.599 00	0.517 89
	$a_{22}$	0.301 16	0.722 96	0.702 73
Equation-of-state background parameters	$\bar{A}_0$	-1	-1	-1
	$\bar{A}_1$	-6.0079	-6.8535	-5.4480
	$\bar{A}_2$	4.5139	3.0974	3.3657
	$\bar{A}_3$	-1.9509	8.4710	-1.4022
	$\bar{A}_4$	5.1371	-19.301	10.499
Caloric background parameters	$d_1$	-0.332 31	-0.383 62	-0.363 55
	$\bar{\mu}_2$	-13.730	-17.949	-15.221
	$\bar{\mu}_3$	-7.9191	-12.115	-9.0252
	$\bar{\mu}_4$	32.249	11.806	-8.6070
	$\bar{\mu}_5$	-93.274		
Note:	$q_D^{-1}$	1.9 Å	1.7 Å	3.2 Å

ty, the equation reproduces the experimental pressures with a reduced  $\chi^2$  of 4.0 in the range bounded by  $\bar{\chi}^{-1} \leq 2.38$ . This reduced  $\chi^2$  is slightly larger than the value 2.3 found by CAS (Ref. 4) for the two-term Landau crossover model in the smaller range bounded by  $\bar{\chi}^{-1} \leq 0.6$ . However, the errors appear to be distributed rather uniformly in the extended range.

A comparison of the crossover equation with the experimental  $C_v$  obtained by Edwards and Buckingham<sup>29</sup> is presented in Fig. 3. The experimental data correspond to two isochores, a critical isochore with  $\rho = \rho_c = 467$  kg/m<sup>3</sup> and an off-critical isochore with  $\rho = 434$  kg/m<sup>3</sup>. The experimental  $C_v$  data along the critical isochore are reproduced by the crossover equation with an average deviation of 1.6%. The transition temperature of the specific-heat data at the off-critical isochore appears to deviate from that at the phase boundary implied by the  $P$ - $\rho$ - $T$  data leading to some systematic deviations within 0.05 K from the transition temperature. However, the equation reproduces the crossover behavior to the classical specific-heat jump at the off-critical isochore well.

The range of validity of the six-term crossover model is sufficiently large so that also contact can be made with the values for  $C_v$  deduced by Michels and de Groot further away from the critical point<sup>35</sup> and shown in Fig. 4.

From the information presented in Figs. 3 and 4 we conclude that the six-term Landau crossover model extends to temperatures and densities sufficiently far away from the critical point where the effect of critical fluctuations on the specific heat has become very small.

The value  $\bar{u} = 0.398$  for CO<sub>2</sub> differs from the value earlier found by CAS (Ref. 4) for the reasons mentioned at the end of Sec. II. However, combined with  $\Lambda = 1.42$  and  $\xi^+ = 1.5$  Å, we find for the physical cutoff  $q_D^{-1}$  a value of 1.9 Å which is essentially the same as the value of 2.0 Å obtained by CAS on the basis of a two-term Landau crossover model.<sup>4</sup>

## B. Steam

As a second example we consider steam. The system-dependent coefficients for the six-term crossover model were determined by the same procedure used previously for the two-term crossover model.<sup>4</sup> The critical parameters were again fixed at the values previously determined by Levelt Sengers *et al.*<sup>36</sup> The other system-dependent coefficients were determined from a fit to the  $P$ - $\rho$ - $T$  data obtained by Rivkin and co-workers,<sup>37,38</sup> except for the caloric background parameters  $\bar{\mu}_j$ , which were determined from a comparison with the speed-of-sound data

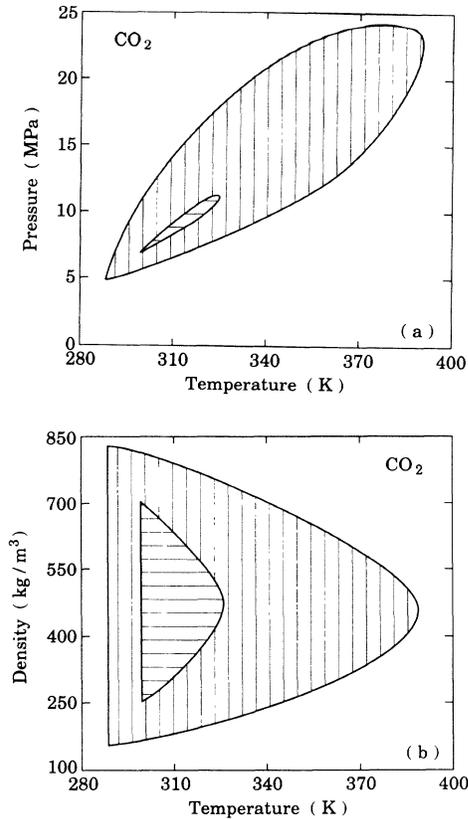


FIG. 1. Range of validity of the crossover model for carbon dioxide (a) in pressure and temperature and (b) in density and temperature. The larger region indicates the range of validity of the six-term Landau crossover model. The smaller region indicates the range of validity when only two terms in the Landau expansion are retained.

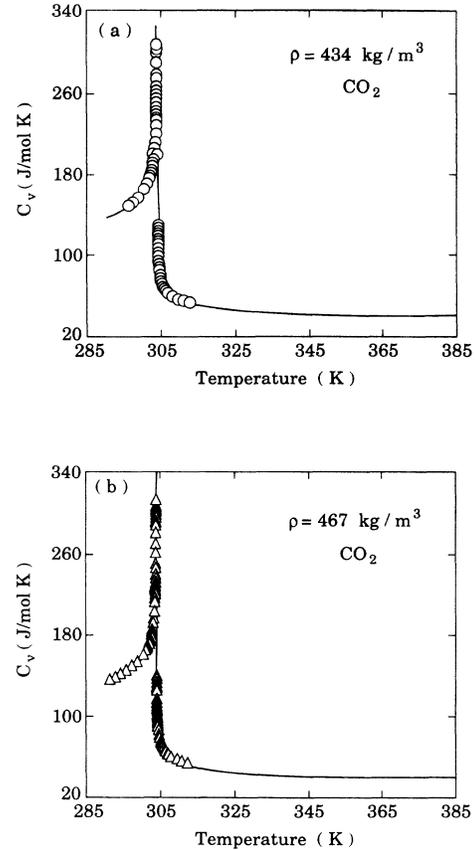


FIG. 3. Isochoric specific heat  $C_v$  of carbon dioxide in the critical region. The data points indicate the experimental data obtained by Edwards and Buckingham (Ref. 29) and the solid curves represent the values calculated from the six-term crossover model.

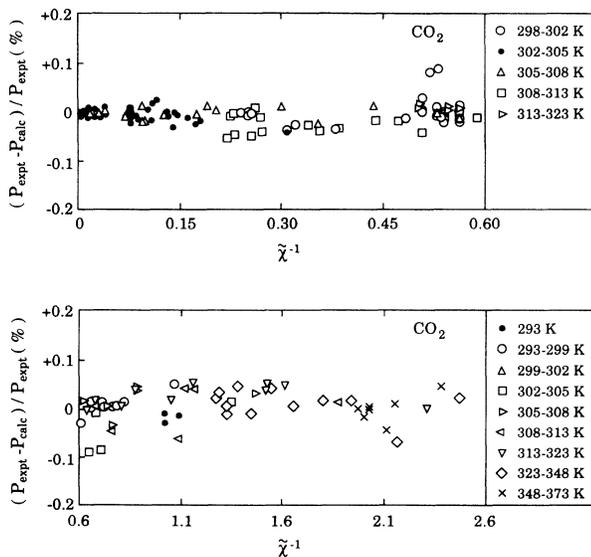


FIG. 2. Percentage differences between the experimental pressures obtained by Michels and co-workers (Refs. 26–28) for carbon dioxide and the values calculated from the six-term crossover model. The deviations are plotted as a function of the inverse susceptibility  $\tilde{\chi}^{-1} = (\partial\bar{\mu}/\partial\bar{p})_T$ .

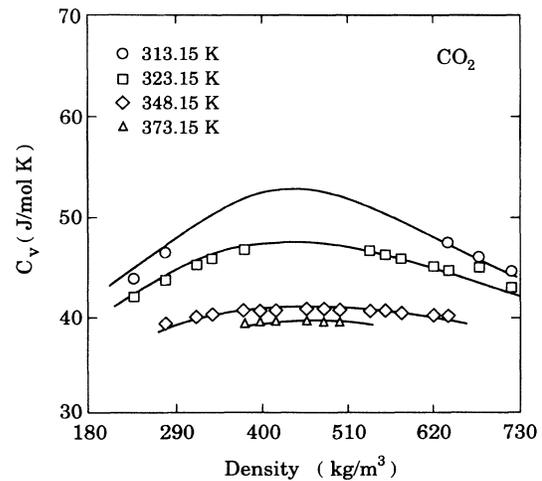


FIG. 4. Isochoric specific heat  $C_v$  of carbon dioxide away from the critical point. The data points are the values deduced by Michels and de Groot (Ref. 35) from the experimental  $P$ - $\rho$ - $T$  data and the solid curves represent the values calculated from the six-term crossover model.

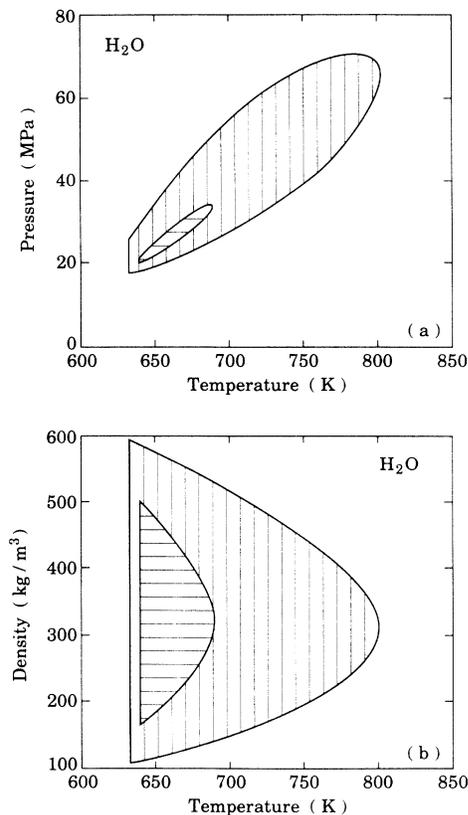


FIG. 5. Range of validity of the crossover model for steam (a) in pressure and temperature and (b) in density and temperature. The larger region indicates the range of validity of the six-term Landau crossover model. The smaller region indicates the range of validity when only two terms in the Landau expansion are retained.

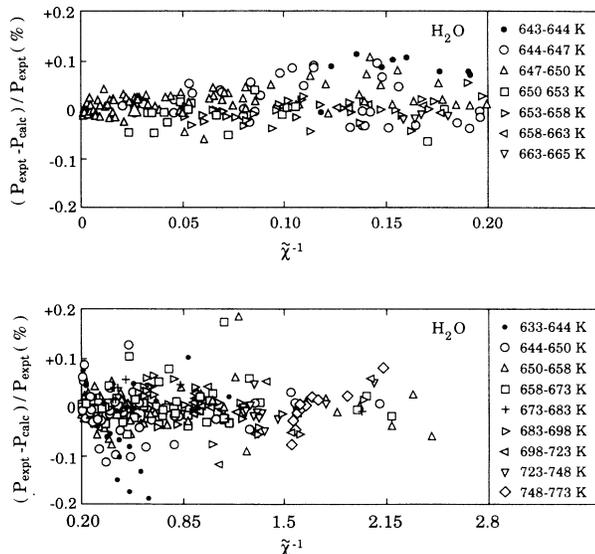


FIG. 6. Percentage differences between the experimental pressures obtained by Rivkin and co-workers (Refs. 37 and 38) for steam and the values calculated from the six-term crossover model. The deviations are plotted as a function of the inverse susceptibility  $\tilde{\chi}^{-1} = (\partial \bar{\mu} / \partial \bar{p})_T$ .

obtained by Erokhin and Kolyanov.<sup>39,40</sup> For details about temperature-scale corrections the reader is referred to previous publications.<sup>36,41</sup> For values of the system-dependent constants for steam are included in Table IV.

The six-term Landau crossover model appears to reproduce the thermodynamic properties of steam in a range of densities and temperatures bounded by

$$\tilde{\chi}^{-1} \leq 2.6, \quad (5.2)$$

which corresponds to a temperature range

$$633 \text{ K} \leq T \leq 773 \text{ K} \quad \text{at } \rho = \rho_c \quad (5.2a)$$

and a density range

$$117 \text{ kg/m}^3 \leq \rho \leq 579 \text{ kg/m}^3 \quad \text{at } T = T_c. \quad (5.2b)$$

The range of validity in a pressure-temperature plane and in a density-temperature plane is shown in Fig. 5. If only two terms are retained in the Landau expansion,<sup>4</sup> the range of validity reduces  $\tilde{\chi}^{-1} \leq 0.5$ .

With  $\sigma_p = 0.001 \text{ MPa}$ ,  $\sigma_T = 0.02 \text{ K}$ , and  $\sigma_\rho = 0.05\%$  as the estimated errors in pressure, temperature, and density, the equation reproduces the experimental pressures of Rivkin and co-workers<sup>37,38</sup> with a reduced  $\chi^2$  of 1.2 in the range bounded by (5.2). A plot of the deviations of the experimental pressures from the calculated pressures is presented in Fig. 6. With  $\xi^+ = 1.3 \text{ \AA}$  for steam, we find  $q_D^{-1} = 1.7 \text{ \AA}$ , slightly larger than the value of  $1.0 \text{ \AA}$  found by CAS on the basis of the two-term Landau crossover model.

A comparison of the six-term Landau crossover model with the experimental speed-of-sound data obtained by Erokhin and Kalyanov<sup>39,40</sup> is shown in Fig. 7, a comparison with the experimental  $C_v$  data obtained by Baehr and Schomäcker<sup>42</sup> is shown in Fig. 8, and a comparison with the experimental  $C_p$  data obtained by Sirota *et al.*<sup>43,44</sup> is shown in Fig. 9. We emphasize that neither the  $C_v$  data of Baehr and Schömacker nor the  $C_p$  data of Sirota *et al.* were used in the determination of any of the system-dependent constants in the crossover equation.

### C. Ethane

As a third example we consider ethane. The reason is that we needed an equation for the thermodynamic properties of ethane in order to interpret new thermal-conductivity measurements for ethane in the critical region.<sup>45</sup> We fixed the critical parameters at the values reported by Douslin and Harrison.<sup>48</sup> The system-dependent constants were determined from a fit to the  $P$ - $\rho$ - $T$  obtained by Douslin and Harrison<sup>46</sup> except for the caloric background constants which were determined from a comparison with the  $C_v$  data obtained by Roder.<sup>47</sup> The values of the system-dependent constants for ethane are included in Table IV. The experimental data of Douslin and Harrison are quite accurate. With estimated errors in pressure, temperature, and density as small as  $\sigma_p = 0.00005 \text{ MPa}$ ,  $\sigma_T = 0.001 \text{ K}$ , and  $\sigma_\rho = 0.15 \text{ kg/m}^3$ , we find that the equation represents the experimental

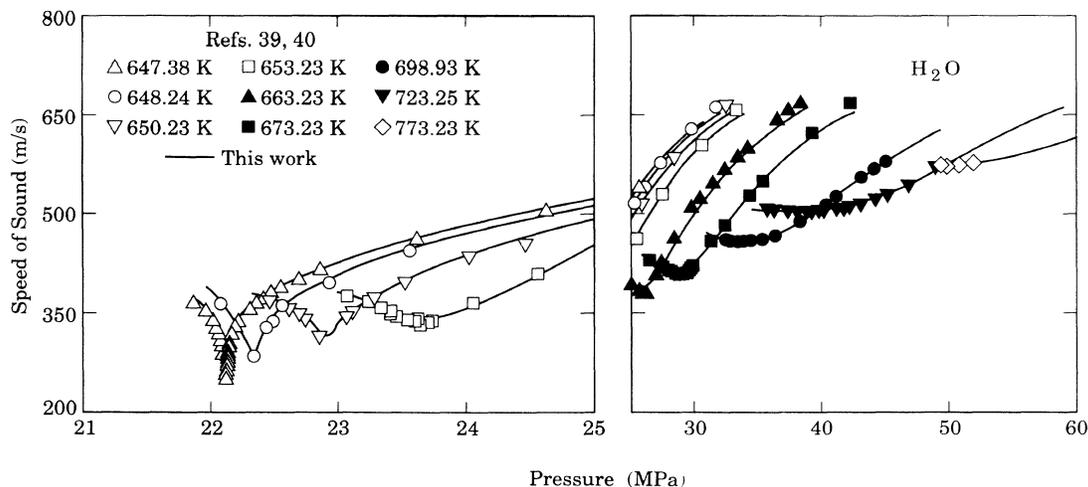


FIG. 7. Thermodynamic sound velocity of steam in the critical region. The data points indicate the experimental values obtained by Erokhin and Kalyanov (Refs. 39 and 40) and the solid curves represent the values calculated from the six-term crossover model.

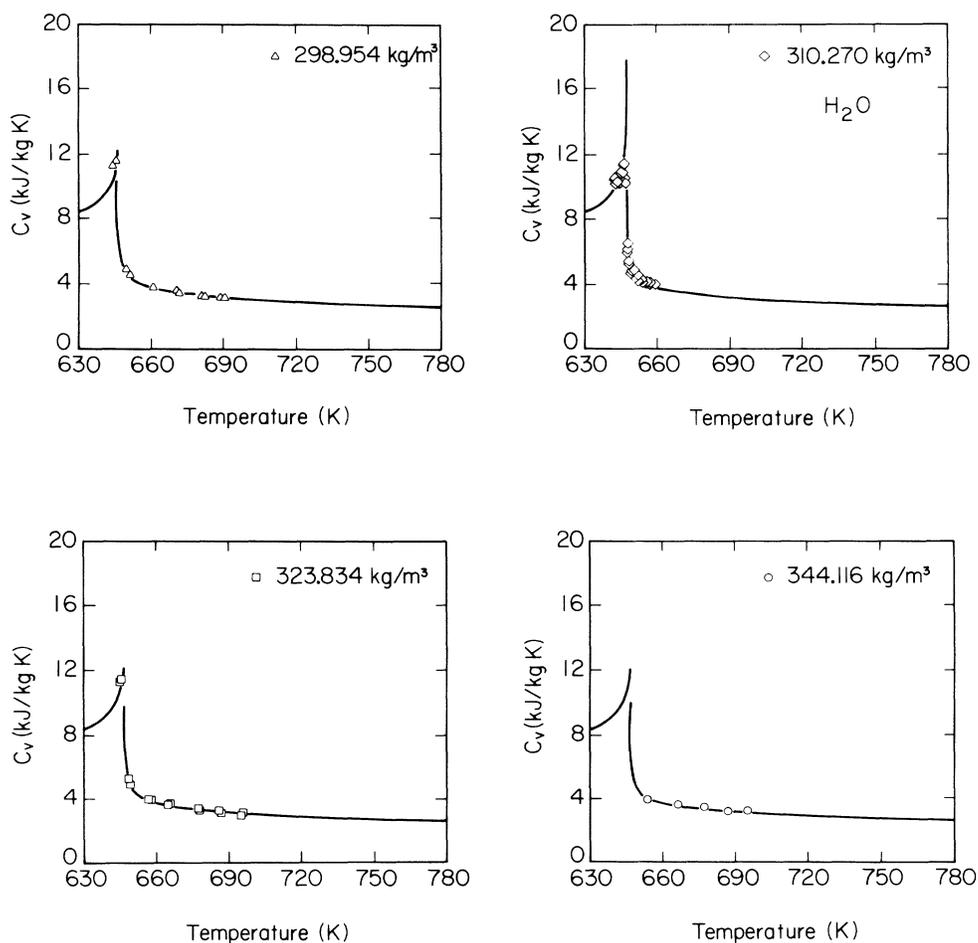


FIG. 8. Isochoric specific heat  $C_v$  of steam in the critical region. The data points indicate the experimental data obtained by Baehr and Schomäcker (Ref. 42) and the solid curves represent the values calculated from the six-term crossover model.

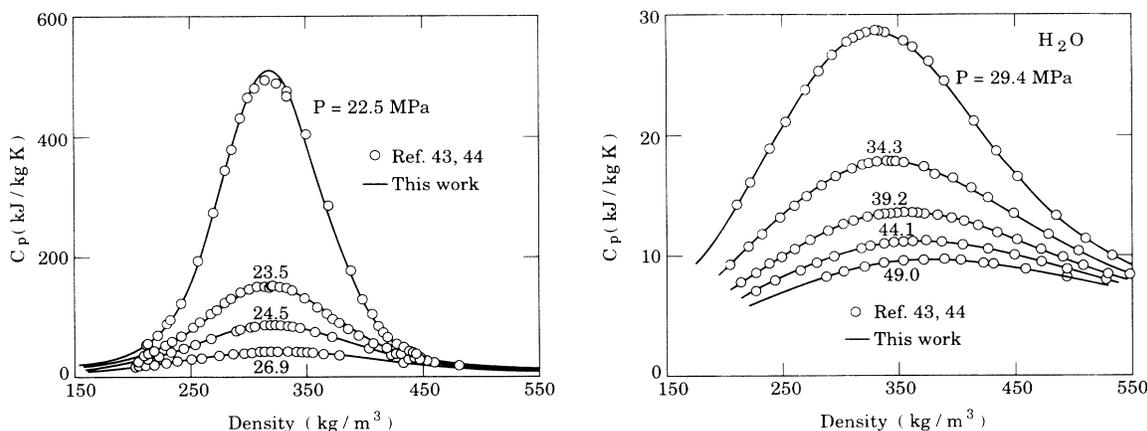


FIG. 9. Isobaric specific heat  $C_p$  of steam in the critical region. The data points indicate the experimental data obtained by Sirota *et al.* (Refs. 43 and 44) and the solid curves represent the values calculated from the six-term crossover model.

pressure data with a standard  $\chi^2$  of 1.2 in a range bounded by

$$\tilde{\chi}^{-1} \leq 2.2, \quad (5.3)$$

which corresponds to a temperature range

$$293 \text{ K} \leq T \leq 373 \text{ K} \quad \text{at } \rho = \rho_c, \quad (5.3a)$$

and a density range

$$84 \text{ kg/m}^3 \leq \rho \leq 340 \text{ kg/m}^3 \quad \text{at } T = T_c. \quad (5.3b)$$

Plots of the deviations of the experimental pressures from the calculated pressures are presented in Fig. 10. With  $\xi^+ = 1.9 \text{ \AA}$  for ethane,<sup>48</sup> we find  $q_D^{-1} = 3.2 \text{ \AA}$ . A

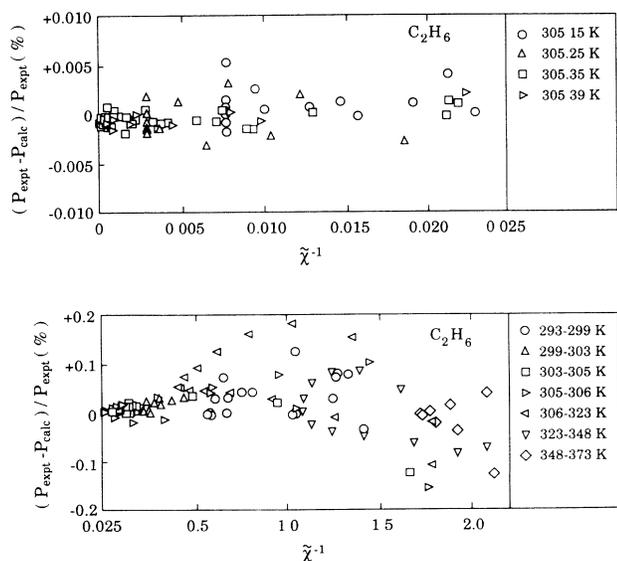


FIG. 10. Percentage differences between the experimental pressures obtained by Douslin and Harrison (Ref. 46) for ethane and the values calculated from the six-term crossover model. The derivations are plotted as a function of the inverse susceptibility  $\tilde{\chi}^{-1} = (\partial \bar{\mu} / \partial \bar{p})_T$ .

comparison with the specific heat data obtained by Roder is shown in Fig. 11. Since the data of Roder were not obtained at strictly constant densities, we have not plotted the  $C_p$  data themselves as previously done for the other fluids, but give a deviation plot. The crossover equation reproduces the experimental  $C_v$  data of Roder inside the range bounded by Eq. (5.3) with an average deviation of 1.3%. A comparison of the crossover model with the experimental  $C_v$  data obtained by Shmakov<sup>49</sup> for ethane is presented in Fig. 12. The critical temperature implied by the  $C_v$  data of Shmakov is 0.033 K higher than the value of  $T_c$  reported by Douslin and Harrison. When a correction is made for this temperature difference, the  $C_v$  data of Shmakov are reproduced by the equation with an average deviation of 1.5%.

Balzarini and co-workers<sup>50-52</sup> have obtained accurate interferometric experimental data for the coexisting liquid and vapor densities  $\rho_l$  and  $\rho_v$  of ethane. A comparison of the crossover equation with these experimental coexisting data is presented in Fig. 13. The agreement is quite satisfactory if one keeps in mind that none of the density data reported by Balzarini and co-workers for ethane at coexistence were used to determine any of the constants in the crossover equation for ethane. Any residual deviations are simply related to a small systematic

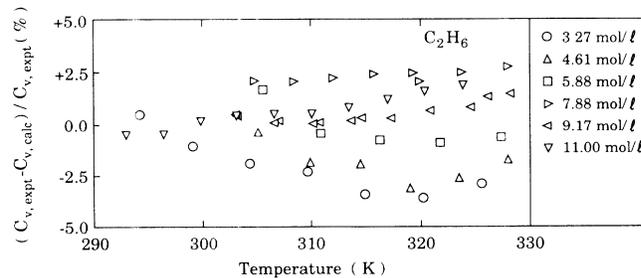


FIG. 11. Percentage difference between the experimental  $C_v$  data obtained by Roder (Ref. 47) for ethane and the values calculated from the six-term crossover model.

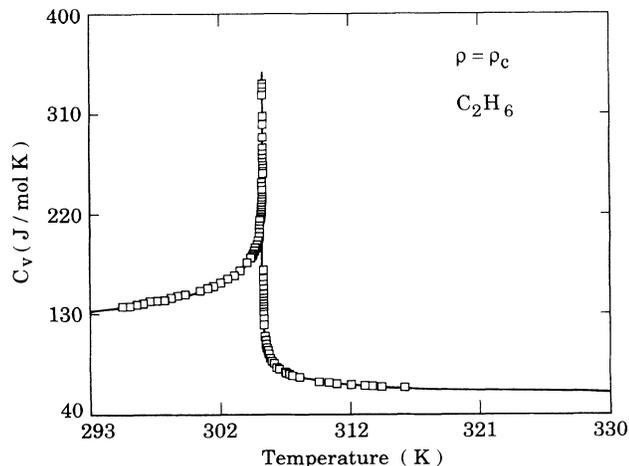


FIG. 12. Isochoric specific heat  $C_v$  of ethane at  $\rho = \rho_c$  as a function of temperature. The data points indicate the experimental data obtained by Shmakov (Ref. 49) and the solid curves represent the values calculated from the six-term crossover model.

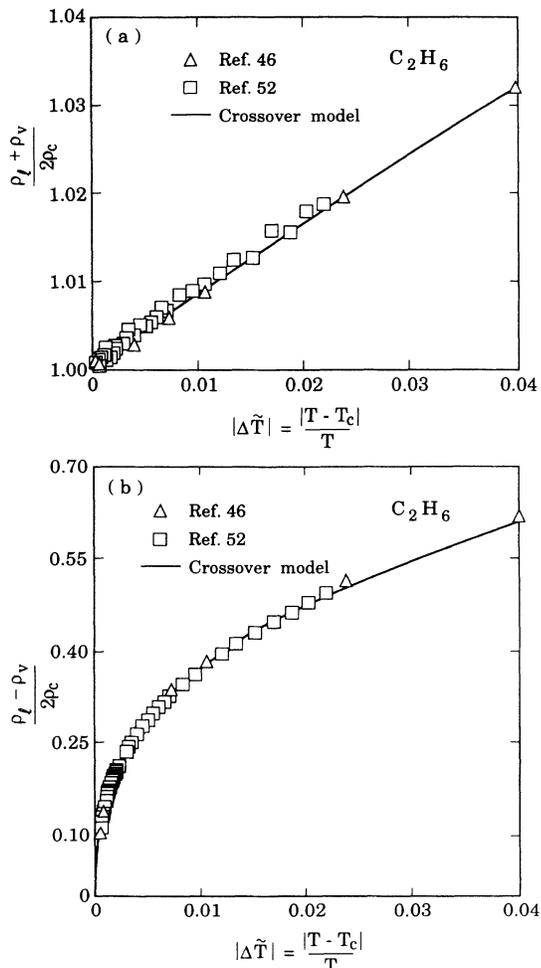


FIG. 13. Coexistence curve  $(\rho_l - \rho_v)/2\rho_c$  and coexistence diameter  $(\rho_l + \rho_v)/2\rho_c$  for ethane as a function of  $\Delta\tilde{T}$ . The triangles indicate the experimental data obtained by Douslin and Harrison (Ref. 46) and the squares indicate the more experimental data reported more recently by Balzarini and co-workers (Ref. 52). The solid curves represent the values from the six-term crossover model.

difference between the experimental data of Balzarini and co-workers and those of Douslin and Harrison. The coexistence-curve diameter satisfies an expression given by (4.2). From the fit of our crossover model to the  $P$ - $\rho$ - $T$  data we obtain for ethane the coefficients  $d_{s1} = 0.356$  for the  $|\Delta\tilde{T}|^{1-\alpha}$  term and  $d_1 = -0.364$  for the term proportional to  $\Delta\tilde{T}$ . In spite of the agreement with the coexistence-curve data of Balzarini and co-workers, these coefficients differ considerably from the values  $d_{s1} = 0.661$  and  $d_1 = -0.150$  deduced by Pestak *et al.*<sup>52</sup> from these coexistence-curve data. These differences are due to the correlation between the  $|\Delta\tilde{T}|^{1-\alpha}$  and the  $\Delta\tilde{T}$  terms which severely hampers a determination of the actual amplitudes from coexistence-curve-diameter data alone. On the other hand, if we try to fit the  $P$ - $\rho$ - $T$  data with  $d_1 = -0.15$ , the standard  $\chi^2$  increases from 1.2 to 69. We conclude that the value of the amplitude of the  $|\Delta\tilde{T}|^{1-\alpha}$  deduced from a restricted set of data should be treated with reservations. A similar observation was made previously in determining amplitudes of correction-to-scaling terms in the critical power-law expansions.<sup>1</sup>

## VI. CONCLUSION

We have developed a procedure to construct from a classical Landau expansion a Helmholtz free-energy density which accounts for the crossover from scaled Ising-like behavior close to the critical point to analytic behavior far away from the critical point. A comparison with experimental data indicates that a satisfactory thermodynamic representation is obtained at almost all temperatures and densities where the effects of critical fluctuations are significant, if only six terms are retained in the classical Landau expansion.

## ACKNOWLEDGMENTS

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## APPENDIX A: THERMODYNAMIC RELATIONS

### 1. Reduced thermodynamic quantities

The reduced thermodynamic quantities are as follows:

$$\tilde{T} = -\frac{T_c}{T}, \quad \tilde{\mu} = \frac{\mu \rho_c T_c}{TP_c}, \quad \tilde{P} = \frac{PT_c}{TP_c},$$

$$\tilde{A}_0(\tilde{T}) = -1 + \sum_{j=1} \tilde{A}_j(\Delta\tilde{T})^j, \quad (\text{A9})$$

$$\tilde{\rho} = \frac{\rho}{\rho_c}, \quad \tilde{A} = \frac{AT_c}{VTP_c}, \quad \tilde{U} = \frac{U}{VP_c},$$

$$\tilde{\mu}_0(\tilde{T}) = \sum_{j=0} \tilde{\mu}_j(\Delta\tilde{T})^j. \quad (\text{A10})$$

(A1)

$$\tilde{S} = \frac{ST_c}{VP_c}, \quad \tilde{H} = \frac{HT_c}{VTP_c}, \quad \tilde{\chi} = \left[ \frac{\partial \tilde{\rho}}{\partial \tilde{\mu}} \right]_T,$$

The term  $\Delta\tilde{A}$  in (A8) is the crossover part of the free-energy density as specified in Appendix B.

$$\tilde{C}_v = \frac{C_v T_c}{VP_c}, \quad \tilde{C}_p = \frac{C_p T_c}{VP_c}, \quad \tilde{W} = W \left[ \frac{\rho_c T_c}{P_c T} \right]^{1/2},$$

#### 4. Derived thermodynamic quantities

The derived thermodynamic quantities are as follows:

where  $T$  is temperature,  $\rho$  is density,  $P$  is pressure,  $\mu$  is chemical potential,  $A$  is Helmholtz free energy,  $U$  is internal energy,  $S$  is entropy,  $H$  is enthalpy,  $C_v$  is isochoric heat capacity,  $C_p$  is isobaric heat capacity, and  $W$  is the speed of sound.

#### 2. Differential relations

The differential relations are

$$d\tilde{A} = -\tilde{U}d\tilde{T} + \tilde{\mu}d\tilde{\rho},$$

$$d\tilde{P} = \tilde{U}d\tilde{T} + \tilde{\rho}d\tilde{\mu},$$

$$d\tilde{S} = -\tilde{T}d\tilde{U} - \tilde{\mu}d\tilde{\rho},$$

$$d\tilde{H} = -\tilde{T}d\tilde{U} + \tilde{\rho}d\tilde{\mu},$$

(A2)

with

$$\tilde{P} = \tilde{\rho}\tilde{\mu} - \tilde{A}, \quad (\text{A3})$$

$$\tilde{S} = -\tilde{T}\tilde{U} - \tilde{A}, \quad (\text{A4})$$

$$\tilde{H} = \tilde{P} - \tilde{T}\tilde{U}. \quad (\text{A5})$$

#### 3. Fundamental equations

The fundamental equations are

$$\Delta\tilde{T} = \tilde{T} + 1, \quad (\text{A6})$$

$$\Delta\tilde{\rho} = \tilde{\rho} - 1, \quad (\text{A7})$$

$$\tilde{A} = \tilde{\rho}\tilde{\mu}_0(\tilde{T}) + \tilde{A}_0(\tilde{T}) + \Delta\tilde{A}, \quad (\text{A8})$$

with

$$\tilde{\mu} = \Delta\tilde{\mu} + \tilde{\mu}_0(\tilde{T}), \quad (\text{A11})$$

$$\Delta\tilde{\mu} = \left[ \frac{\partial \Delta\tilde{A}}{\partial \Delta\tilde{\rho}} \right]_{\Delta\tilde{T}}, \quad (\text{A12})$$

$$\tilde{\chi}^{-1} = \left[ \frac{\partial^2 \Delta\tilde{A}}{\partial \Delta\tilde{\rho}^2} \right]_{\Delta\tilde{T}}, \quad (\text{A13})$$

$$\tilde{U} = -\frac{d\tilde{A}_0(\tilde{T})}{d\tilde{T}} - \tilde{\rho} \frac{d\tilde{\mu}_0(\tilde{T})}{d\tilde{T}} - \left[ \frac{\partial \Delta\tilde{A}}{\partial \Delta\tilde{T}} \right]_{\Delta\tilde{\rho}}, \quad (\text{A14})$$

$$\left[ \frac{\partial \tilde{P}}{\partial \tilde{T}} \right]_{\tilde{\rho}} = -\frac{d\tilde{A}_0(\tilde{T})}{d\tilde{T}} + \tilde{\rho} \frac{\partial^2 \Delta\tilde{A}}{\partial \Delta\tilde{\rho} \partial \Delta\tilde{T}} - \left[ \frac{\partial \Delta\tilde{A}}{\partial \Delta\tilde{T}} \right]_{\Delta\tilde{\rho}}, \quad (\text{A15})$$

$$\tilde{C}_v / \tilde{T}^2 = -\frac{d^2 \tilde{A}_0(\tilde{T})}{d\tilde{T}^2} - \tilde{\rho} \frac{d^2 \tilde{\mu}_0(\tilde{T})}{d\tilde{T}^2} - \left[ \frac{\partial^2 \Delta\tilde{A}}{\partial \Delta\tilde{T}^2} \right]_{\Delta\tilde{\rho}}, \quad (\text{A16})$$

$$\tilde{C}_p = \tilde{C}_v + \frac{\tilde{\chi}}{\tilde{\rho}^2} \left[ \tilde{P} - \tilde{T} \left[ \frac{\partial \tilde{P}}{\partial \tilde{T}} \right]_{\tilde{\rho}} \right]^2, \quad (\text{A17})$$

$$\tilde{W} = \left[ \frac{\tilde{\rho} \tilde{C}_p}{\tilde{\chi} \tilde{C}_v} \right]^{1/2}. \quad (\text{A18})$$

### APPENDIX B: EQUATIONS FOR SIX-TERM LANDAU CROSSOVER MODEL

#### 1. Fundamental equations

The fundamental equations are the following:

$$t = c_t \Delta \tilde{T} + c \left[ \frac{\partial \Delta \tilde{A}_r}{\partial M} \right]_t, \quad (\text{B1})$$

$$M = c_\rho (\Delta \tilde{\rho} - d_1 \Delta \tilde{T}) + c \left[ \frac{\partial \Delta \tilde{A}_r}{\partial t} \right]_M, \quad (\text{B2})$$

$$\Delta \tilde{A} = \Delta \tilde{A}_r - c \left[ \frac{\partial \Delta \tilde{A}_r}{\partial M} \right]_t \left[ \frac{\partial \Delta \tilde{A}_r}{\partial t} \right]_M, \quad (\text{B3})$$

$$\begin{aligned} \Delta \tilde{A}_r = & \frac{1}{2} t M^2 \mathcal{T} \mathcal{D} + \frac{1}{4!} u \Lambda M^4 \mathcal{D}^2 \mathcal{U} + \frac{1}{5!} a_{05} M^5 \mathcal{D}^{5/2} \mathcal{V} \mathcal{U} \\ & + \frac{1}{6!} a_{06} M^6 \mathcal{D}^3 \mathcal{U}^{3/2} + \frac{1}{4!} a_{14} t M^4 \mathcal{T} \mathcal{D}^2 \mathcal{U}^{1/2} \\ & + \frac{1}{2!} a_{22} t^2 M^2 \mathcal{T}^2 \mathcal{D} \mathcal{U}^{-1/2} - \frac{1}{2} t^2 \mathcal{H}, \end{aligned} \quad (\text{B4})$$

$$\mathcal{T} = Y^{(2-\nu^{-1})/\omega}, \quad (\text{B5})$$

$$\mathcal{D} = Y^{-\eta/\omega}, \quad (\text{B6})$$

$$\mathcal{V} = Y^{(2\omega_a - 1)/2\omega}, \quad (\text{B7})$$

$$\mathcal{U} = Y^{1/\omega}, \quad (\text{B8})$$

$$\mathcal{H} = \frac{\nu}{\alpha \bar{u} \Lambda} (Y^{-\alpha/\nu\omega} - 1), \quad (\text{B9})$$

where the crossover function  $Y$  is to be determined from

$$1 - (1 - \bar{u})Y = \bar{u} [1 + (\Lambda/\kappa)^2]^{1/2} Y^{1/\omega}, \quad (\text{B10})$$

with

$$\kappa^2 = t \mathcal{T} + \frac{1}{2} u \Lambda \mathcal{U} M^2 \mathcal{D}. \quad (\text{B11})$$

## 2. Thermodynamic derivatives

The thermodynamic derivatives are

$$\left[ \frac{\partial \Delta \tilde{A}}{\partial \Delta \tilde{\rho}} \right]_{\Delta \tilde{T}} = c_\rho \left[ \frac{\partial \Delta \tilde{A}_r}{\partial M} \right]_t, \quad (\text{B12})$$

$$\left[ \frac{\partial \Delta \tilde{A}}{\partial \Delta \tilde{T}} \right]_{\Delta \tilde{\rho}} = c_t \left[ \frac{\partial \Delta \tilde{A}_r}{\partial t} \right]_M - c_\rho d_1 \left[ \frac{\partial \Delta \tilde{A}_r}{\partial M} \right]_t, \quad (\text{B13})$$

$$\left[ \frac{\partial^2 \Delta \tilde{A}}{\partial \Delta \tilde{\rho}^2} \right]_{\Delta \tilde{T}} = c_\rho^2 \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial M^2} \right]_t G^{-1}, \quad (\text{B14})$$

$$\frac{\partial^2 \Delta \tilde{A}}{\partial \Delta \tilde{\rho} \partial \Delta \tilde{T}} = c_\rho c_t \left\{ \frac{\partial^2 \Delta \tilde{A}_r}{\partial t \partial M} - c \left[ \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial t \partial M} \right]^2 - \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial t^2} \right]_M \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial M^2} \right]_t \right\} G^{-1} - c_\rho^2 d_1 \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial M^2} \right]_t G^{-1}, \quad (\text{B15})$$

$$\begin{aligned} \left[ \frac{\partial^2 \Delta \tilde{A}}{\partial \Delta \tilde{T}^2} \right]_{\Delta \tilde{\rho}} = & c_t^2 \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial t^2} \right]_M G^{-1} - 2c_t c_\rho d_1 \left\{ \frac{\partial^2 \Delta \tilde{A}_r}{\partial t \partial M} - c \left[ \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial t \partial M} \right]^2 - \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial t^2} \right]_M \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial M^2} \right]_t \right\} G^{-1} \\ & + c_\rho^2 d_1^2 \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial M^2} \right]_t G^{-1}, \end{aligned} \quad (\text{B16})$$

with

$$G = \left[ 1 - c \frac{\partial^2 \Delta \tilde{A}_r}{\partial t \partial M} \right]^2 - c^2 \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial t^2} \right]_M \left[ \frac{\partial^2 \Delta \tilde{A}_r}{\partial M^2} \right]_t. \quad (\text{B17})$$

## 3. Derivatives of crossover functions

The derivatives of crossover functions are the following:

$$\left[ \frac{\partial \kappa^2}{\partial t} \right]_M = F_1(t, M) \mathcal{T}, \quad (\text{B18})$$

$$\left[ \frac{\partial \kappa^2}{\partial M} \right]_t = F_1(t, M) u \Lambda M \mathcal{U} \mathcal{D}, \quad (\text{B19})$$

$$\left[ \frac{\partial Y}{\partial t} \right]_M = F_2(t, M) \mathcal{T}, \quad (\text{B20})$$

$$\left[ \frac{\partial Y}{\partial M} \right]_t = F_2(t, M) u \Lambda M \mathcal{U} \mathcal{D}, \quad (\text{B21})$$

with

$$F_1 = (1 + f_1 f_2)^{-1}, \quad (\text{B22})$$

$$F_2 = f_1 Y F_1, \quad (\text{B23})$$

$$f_1 = \frac{\Lambda^2}{2\kappa^4} \left[ 1 + \frac{\Lambda^2}{\kappa^2} \right]^{-1} \left[ \frac{1}{\omega} + \frac{(1-\bar{u})Y}{1-(1-\bar{u})Y} \right]^{-1}, \quad (\text{B24})$$

$$f_2 = - \left[ \frac{2-\nu^{-1}}{\omega} \right] t \mathcal{T} + \left[ \frac{1-\eta}{2\omega} \right] u \Lambda M^2 \mathcal{U} \mathcal{D}. \quad (\text{B25})$$

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- <sup>1</sup>For a review see J. V. Sengers and J. M. H. Levelt Sengers, *Ann. Rev. Phys. Chem.* **37**, 189 (1986).
- <sup>2</sup>M. E. Fisher, in *Critical Phenomena*, Vol. 186 of *Lecture Notes in Physics*, edited by F. J. W. Hahne (Springer-Verlag, Berlin, 1982), p. 1.
- <sup>3</sup>J. M. H. Levelt Sengers and J. V. Sengers, in *Perspectives in Statistical Physics*, edited by H. J. Raveché (North-Holland, Amsterdam, 1981), p. 239.
- <sup>4</sup>Z. Y. Chen, P. C. Albright, and J. V. Sengers, *Phys. Rev. A* **41**, 3161 (1990).
- <sup>5</sup>J. F. Nicoll, *Phys. Rev. A* **24**, 2203 (1981).
- <sup>6</sup>A. A. Patashinskii and V. I. Pokrovskii, *Fluctuation Theory of Phase Transitions* (Pergamon, New York, 1979).
- <sup>7</sup>E. Brézin, J. C. Le Guillou, and J. Zinn-Justin, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, New York, 1976), Vol. 6, p. 125.
- <sup>8</sup>A. P. Bruce and D. J. Wallace, *J. Phys. A* **9**, 1117 (1976).
- <sup>9</sup>J. F. Nicoll and P. C. Albright, *Phys. Rev. B* **31**, 4576 (1985).
- <sup>10</sup>J. F. Nicoll and J. K. Bhattacharjee, *Phys. Rev. B* **23**, 389 (1981).
- <sup>11</sup>D. Z. Albert, *Phys. Rev. B* **25**, 4810 (1982).
- <sup>12</sup>J. C. Le Guillou and J. Zinn-Justin, *J. Phys. (Paris) Lett.* **46**, L137 (1985); *J. Phys. (Paris)* **48**, 19 (1987).
- <sup>13</sup>A. J. Liu and M. E. Fisher, *Physica A* **136**, 35 (1989).
- <sup>14</sup>R. Schloms and V. Dohm, *Nucl. Phys. B* **328**, 639 (1989).
- <sup>15</sup>Z. Y. Chen, *Phys. Rev. B* **40**, 4656 (1989).
- <sup>16</sup>C. Bervillier, *Phys. Rev. B* **34**, 8141 (1986).
- <sup>17</sup>C. Bervillier and C. Godrèche, *J. Phys. (Paris)* **43**, 243 (1982).
- <sup>18</sup>C. Bagnuls, C. Bervillier, D. I. Meiron, and B. G. Nickel, *Phys. Rev. B* **35**, 3585 (1987).
- <sup>19</sup>M. Ley-Koo and M. S. Green, *Phys. Rev. A* **23**, 2650 (1981).
- <sup>20</sup>F. C. Zhang and R. K. P. Zia, *J. Phys. A* **15**, 3303 (1982).
- <sup>21</sup>J. F. Nicoll and P. C. Albright, in *Proceedings of the Eighth Symposium on Thermophysical Properties*, edited by J. V. Sengers (American Society of Mechanical Engineers, New York, 1982), Vol. I, p. 377.
- <sup>22</sup>R. F. Kayser and H. J. Raveché, *Phys. Rev. A* **29**, 1013 (1984).
- <sup>23</sup>P. C. Albright, J. V. Sengers, J. F. Nicoll, and M. Ley-Koo, *Int. J. Thermophys.* **7**, 75 (1986).
- <sup>24</sup>M. Ley-Koo and M. S. Green, *Phys. Rev. A* **16**, 2483 (1977).
- <sup>25</sup>P. C. Albright, Z. Y. Chen, and J. V. Sengers, *Phys. Rev. B* **36**, 877 (1987).
- <sup>26</sup>A. Michels and C. Michels, *Proc. R. Soc. London Ser. A* **153**, 201 (1935).
- <sup>27</sup>A. Michels, C. Michels, and H. Wouters, *Proc. R. Soc. London Ser. A* **153**, 214 (1935).
- <sup>28</sup>A. Michels, B. Blaisse, and C. Michels, *Proc. R. Soc. London Ser. A* **160**, 358 (1937).
- <sup>29</sup>T. J. Edwards, Ph.D. thesis, University of Western Australia, 1984.
- <sup>30</sup>P. C. Albright, T. J. Edwards, Z. Y. Chen, and J. V. Sengers, *J. Chem. Phys.* **87**, 1717 (1987).
- <sup>31</sup>M. R. Moldover, *J. Chem. Phys.* **61**, 1766 (1974).
- <sup>32</sup>G. Morrison (private communication).
- <sup>33</sup>*Metrologia* **5**, 35 (1969).
- <sup>34</sup>J. M. H. Levelt Sengers and W. T. Chen, *J. Chem. Phys.* **56**, 595 (1972).
- <sup>35</sup>A. Michels and S. R. de Groot, *Appl. Sci. Res. A* **1**, 94 (1948).
- <sup>36</sup>J. M. H. Levelt Sengers, B. Kamgar-Parsi, F. W. Balfour, and J. V. Sengers, *J. Phys. Chem. Ref. Data* **12**, 1 (1983).
- <sup>37</sup>S. L. Rivkin, T. S. Akhundov, *Teploenergetika* **9** (1), 57 (1962); **10** (9), 66 (1963).
- <sup>38</sup>S. L. Rivkin, T. S. Akhundov, E. A. Kremnevskaya, and N. N. Asadulaeva, *Teploenergetika* **13** (4), 59 (1966) [*Therm. Eng. (USSR)* **13** (4), 77 (1966)].
- <sup>39</sup>N. F. Erokhin and B. I. Kalyanov, *High Temp.* **17**, 245 (1979).
- <sup>40</sup>N. F. Erokhin and B. I. Kalyanov, *Teploenergetika* **27** (11), 50 (1980) [*Therm. Eng. (USSR)* **27** (11), 634 (1980)].
- <sup>41</sup>J. V. Sengers, J. M. H. Sengers, and B. Kamgar-Parsi, *Stojnický Časopis* **36**, 277 (1985).
- <sup>42</sup>H. D. Baehr and H. Schomäcker, *Forsch. Ingenieurwes.* **41**, 43 (1975).
- <sup>43</sup>A. M. Sirota and B. K. Maltsev, *Teploenergetika* **9** (11), 52 (1962).
- <sup>44</sup>A. M. Sirota, B. K. Maltsev, and P. F. Belyakova, *Teploenergetika* **10** (5), 64 (1963).
- <sup>45</sup>R. Mostert, H. R. van den Berg, P. S. van der Gulik, and J. V. Sengers, *J. Chem. Phys.* **92**, 5454 (1990).
- <sup>46</sup>D. R. Douslin and R. H. Harrison, *J. Chem. Thermodyn.* **5**, 491 (1973).
- <sup>47</sup>H. M. Roder, *J. Res. Natl. Bur. Stand. Sec. A* **80**, 739 (1976).
- <sup>48</sup>G. A. Olchoway and J. V. Sengers, *Intern. J. Thermophys.* **10**, 417 (1989).
- <sup>49</sup>N. G. Shmakov, *Teplofiz. Svoistva Veshchestv Mater.* **7**, 155 (1973).
- <sup>50</sup>M. Burton and D. Balzarini, *Can. J. Phys.* **52**, 2011 (1974).
- <sup>51</sup>D. Balzarini and M. Burton, *Can. J. Phys.* **57**, 1516 (1979).
- <sup>52</sup>M. W. Pestak, R. E. Goldstein, M. H. W. Chan, J. R. de Bruyn, D. A. Balzarini, and N. W. Ashcroft, *Phys. Rev. B* **36**, 599 (1987).