PHYSICAL REVIEW A VOLUME 41, NUMBER 6 15 MARCH 1990

Crossover from singular critical to regular classical thermodynamic behavior of fluids

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(Received 11 August 1989)

A procedure is presented for constructing a thermodynamic free energy for fluids in the critical region that incorporates the crossover from Ising-like singular behavior near the critical point to regular classical behavior far away from the critical point. The procedure is based on an approximation of the solution of the renormalization-group theory of critical phenomena, modified to include effects from a cutoff wave number for the crossover to the classical limit. As an illustration we show how the procedure can be applied to a truncated classical Landau expansion. The results are compared with experimental thermodynamic-property data for carbon dioxide, steam, and ethylene in the critical region.

I. INTRODUCTION

The modern theory of critical-point phase transitions predicts that asymptotically close to the critical point the thermodynamic properties of a system exhibit singular power-law behavior characterized by universal exponents and universal scaling functions.[1,2] Fluids near the vapor-liquid critical point are assumed to belong to the universality class of three-dimensional Ising-like systems.[3,4] However, the region where the asymptotic power-law behavior applies is quite small[5] and correction-to-scaling terms[6] have to be introduced in order to compare the theory with thermodynamic-property data in a finite range around the critical point.[7] On the other hand, outside the critical region various analytic equations of state are used to represent the thermodynamic properties of a fluid from the ideal-gas limit to the high-density limit.[8] Such analytic equations of state have an analytic (mean-field) Landau expansion near the critical point and fail to describe the singular thermodynamic behavior of fluids in the critical region.[9]

Very close to the critical point the Helmholtz free-energy density, i.e., the Helmholtz free energy A per unit of volume V, can be separated into a regular and a singular part. The singular part $\Delta\tilde{A}$ of the Helmholtz free-energy density $\tilde{A}$, made dimensionless as specified in Appendix A, becomes a generalized homogeneous function of its arguments which implies that the number of independent variables can be reduced by scaling. Asymptotically close to the critical point $\Delta\tilde{A}$ can be written in the form[2]

$$\Delta\tilde{A}=\Delta\tilde{A}(t,M)=|t|^{2-\alpha}\Phi(M/|t|^{\beta}) , \tag{1.1}$$

where α and β are universal critical exponents and Φ, apart from an amplitude, is a universal scaling function. Here the variable t is proportional to the difference between the temperature T and the critical temperature T_c, while M is the order parameter which, for fluids, becomes asymptotically proportional to the difference between the actual density ρ and the critical density ρ_c. Near the critical point the correlation length ξ is much larger than any microscopic length q_D^{-1} and higher-order terms in $(q_D\xi)^{-1}$ are neglected. The scaling law (1.1) is the first term of a so-called Wegner series, which has the form

$$\Delta\tilde{A}=|t|^{2-\alpha}\Phi(M/|t|^{\beta})[1+(q_D\xi)^{-\omega_1}\Phi_1(M/|t|^{\beta}) +(q_D\xi)^{-\omega_2}\Phi_2(M/|t|^{\beta})+\cdots] , \tag{1.2}$$

where $\omega_1,\omega_2,\ldots$ are correction-to-scaling exponents and where Φ_1 and Φ_2, apart from their amplitudes, are universal correction-to-scaling functions.

To represent thermodynamic-property data of fluids near the critical point one customarily uses for the scaling function Φ in (1.1) approximate expressions in terms of parametric variables[9-11] which, to a certain degree, are supported by the renormalization-group theory of critical phenomena.[12,13] A popular parametric equation used for this purpose is the so-called linear model.[9,14] The linear-model parametric equation can be extended to include the leading Wegner correction and revised to account for the asymptotic asymmetry of fluids near the critical point.[15] Such an extended and revised linear model can represent the thermodynamic properties near the critical point accurately.[16-18] Specifically, inclusion of the first Wegner correction is necessary to represent the data in terms of the theoretically predicted universal critical exponents[5] rather than in terms of effective empirical exponents.[9,19] However, the range of validity of the scaled equations is still rather restricted and the agreement with experimental data deteriorates very rapidly as soon as these equations are extrapolated outside the near-critical region. The problem is that these scaled equations do not extrapolate properly to any known analytic behavior away from the critical point, neither at low or high densities nor at low or high temperatures. Furthermore, the critical fluctuations also induce nonscaling analytic terms in the free energy which are not properly included in the Wegner series and, hence, in the parametric models.[13,20,21]

The challenge is 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. Near the critical point the cooperative effect of the long-range critical fluctuations determines the asymptotic singular thermodynamic behavior. These fluctuations correspond to $q_D\xi \gg 1$. When the system moves away from the critical region, this inequality no longer applies and crossover to regular behavior takes place when $q_D\xi$ becomes of order unity.[13] Specifically in this article we want to formulate a crossover model that has a theoretical basis and that includes the following features.[4,22,23]

(a) The crossover model should recover the asymptotic scaling laws near the critical point with a realistic estimate of the leading Wegner corrections, and merge into the analytic behavior far away from the critical point.

(b) As mentioned previously, the critical fluctuations not only produce a singular free energy, but also yield an analytic contribution to the free energy.[20,21] This nonscaling feature of the free energy must be properly incorporated to account for, e.g., the crossover behavior of the specific heat from its singularity at the critical point to its jumplike behavior in the classical limit.

(c) Classical equations that represent data away from the critical point imply critical parameters, in particular a critical temperature, that differ from those of the actual critical point.[24] A satisfactory crossover model should recover regular thermodynamic behavior far from the critical point including the shift of the critical temperature from an apparent classical value to its actual fluctuation-induced experimental value.

Some empirical attempts have been made to deal with this crossover problem. A brute-force method was originally attempted by Chapela and Rowlinson[24] in which the scaled equation for the near-critical region was connected to a classical equation outside the critical region with the aid of a switching function. However, it was demonstrated by Woolley that use of a switching function for blending two fundamental equations necessarily leads to spurious behavior of the derivatives of the thermodynamic surface in the crossover regime.[25] Another empirical method has been proposed by Fox in which the crossover from a classical equation outside the critical region to a scaled equation near the critical point is accomplished by an appropriate redefinition of the variables in the classical equation.[26,27] The empirical procedure of Fox avoids the pitfalls of the switching-function approach, but it still does not include the features for a crossover model mentioned above.

A theoretical approach to deal with the crossover problem on the basis of the renormalization-group theory of critical phenomena was pioneered by Rudnick and Nelson[28] and Bruce and Wallace,[29] followed by the work of Nicoll and co-workers,[13,30] Bagnuls and co-workers,[31–34] and Dohm and co-workers.[35–41] Bagnuls and co-workers have made a comparison of their theory with experimental data for xenon, but the comparison was restricted to the temperature dependence of the thermodynamic properties at the critical isochore only.[32] Dohm and co-workers have analyzed the nonasymptotic behavior of the thermodynamic properties of ^{4}He near the superfluid phase transition.[35–40]

Inspired by the previous theoretical results of Nicoll and co-workers[13,30] we develop in this paper a procedure for constructing a crossover free energy for fluids in the critical region, which satisfies all the features listed above and which can be used for a quantitative analysis of experimental thermodynamic-property data as a function of both temperature and density. A slightly less sophisticated version of this work was presented in a previous Rapid Communication.[42]

II. THEORY

A theoretical treatment of the crossover behavior of systems in the critical region can be deduced from the renormalization-group theory of critical phenomena with the aid of so-called match-point methods.[29,30] In this section we briefly review the main features of this method. It is assumed that the effect of critical fluctuations in a (symmetric) Ising-like system in d dimensions can be represented by a Landau-Ginzburg-Wilson (LGW) Hamiltonian of the form[43]

$$H_{\mathrm{LGW}}=\int_{\Lambda}\mathcal{H}(\phi(\mathbf{x}))d^dx\ , \tag{2.1}$$

with

$$\mathcal{H}=\tfrac{1}{2}t\phi^2+\tfrac{1}{2}(\nabla\phi)^2+\frac{u\Lambda^{4-d}}{4!}\phi^4-h\phi\ . \tag{2.2}$$

Here t is the temperature-like field, $\phi(\mathbf{x})$ is the fluctuating order parameter whose average value yields M, u is the ϕ^4-theory coupling constant rescaled by Λ^{4-d}, h is the ordering field and Λ is an ultraviolet cutoff. The relationship of this Hamiltonian to that suitable for the description of the properties of fluids in the critical region has been discussed by several authors.[44–46] The application of the theory to fluids will be further considered in Sec. IV.

Near the critical point the correlation length ξ becomes much larger than any microscopic length and, hence, it is assumed that near the critical point the cutoff Λ can be taken to be infinite. In field theory, the partition function associated with the LGW Hamiltonian (2.1) is a generalization of the Green function which can be specified with the aid of diagrammatic expansions.[1,47,48] Here we only mention some results of the theory without technical details.

The Helmholtz free energy $\Delta\tilde{A}_s$ associated with the LGW Hamiltonian depends on the variables t and M, on the coupling constant u, and on the cutoff wave number Λ. When Λ is taken to be infinite, the variables t and M and the constant u have to be renormalized in order to keep the renormalized Helmholtz free energy finite and independent of the cutoff Λ (the free energy also receives an additive renormalization constant proportional to t^2). The physical Helmholtz free-energy density $\Delta\tilde{A}_s$ is related to the renormalized one as

$$\Delta\tilde{A}_s(t,M;u,\Lambda)=\Delta\tilde{A}_{\mathrm{ren}}(Z_t^{-1}t,Z_M^{-1/2}M,Z_u^{-1}u) -\tfrac{1}{2}(Z_t^{-1}t)^2\Lambda^{-(4-d)}B'(u)\ , \qquad (2.3)$$

where Z_t, Z_M, and Z_u are rescaling factors and where $B'(u)$ is a function which arises from the additive renormalization of the specific heat.[43] The renormalized Helmholtz free energy $\Delta\tilde{A}_{\mathrm{ren}}$ is kept finite in the limit $\Lambda\rightarrow\infty$ by a suitable choice of the rescaling constants Z_i ($i=t,M,u$), which are generally functions of u, Λ, and the dimensionality of the system. The existence of a renormalized theory and the fact that the leading terms of $\Delta\tilde{A}_{\mathrm{ren}}$ are independent of the cutoff implies[47]

$$\Lambda\left[\frac{\partial\Delta\tilde{A}_{\mathrm{ren}}}{\partial\Lambda}\right]_{t_r,M_r,u_r}\simeq 0\ , \qquad (2.4)$$

where $t_r=Z_t^{-1}t$, $M_r=Z_M^{-1/2}M$, and $u_r=Z_u^{-1}u$ are the renormalized variables. Equation (2.4) is only correct close to the critical point, where terms of order t/Λ^2 which appear at the right-hand side of (2.4), can be neglected. If (2.3) is inserted into (2.4), one obtains a partial differential equation of the form[43,44,47]

$$\left[\Lambda\frac{\partial}{\partial\Lambda}+\beta(u)\frac{\partial}{\partial u}+\left[2-\frac{1}{\nu(u)}\right]t\frac{\partial}{\partial t} -\frac{1}{2}\eta(u)M\frac{\partial}{\partial M}\right]\Delta\tilde{A}_s+\tfrac{1}{2}t^2\Lambda^{-(4-d)}B(u)=0 \qquad (2.5)$$

with

$$\eta(u)=-\Lambda\frac{\partial\ln Z_M}{\partial\Lambda}\ , \qquad (2.6a)$$

$$\beta(u)=u\Lambda\frac{\partial\ln Z_u}{\partial\Lambda}\ , \qquad (2.6b)$$

$$2-\frac{1}{\nu(u)}=\Lambda\frac{\partial\ln Z_t}{\partial\Lambda}\ , \qquad (2.6c)$$

and where $B(u)$, related to $B'(u)$ in (2.3), is a function of order unity.[43] The last term on the left-hand side of (2.5) includes a fluctuation-induced analytic term[49] proportional to t^2.

The renormalization equation (2.5) has been studied by many authors. Nicoll and co-workers[13,30] have applied the equation to develop a crossover theory using an expansion in terms of $\epsilon=4-d$. Bagnuls and co-workers[31-34] have considered the solution of a similar equation for three-dimensional systems. Dohm and co-workers have studied the solution of a similar equation for the thermodynamic properties of ^{4}He near the superfluid phase transition.[35-41]

The renormalization equation (2.5) is a first-order partial differential equation which can be solved formally by the method of characteristics and the solution can be written in the form[13,30]

$$\Delta\tilde{A}_s(t,M,u,\Lambda)=\Delta\tilde{A}_s(t\mathcal{T}(l),M\mathcal{D}^{1/2}(l),u(l),\Lambda(l)) -\tfrac{1}{2}t^2\mathcal{K}(l) \qquad (2.7)$$

with

$$\Lambda(l)=\Lambda e^{-l}\ . \qquad (2.8)$$

The characteristic equation is

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

with the boundary condition

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

The rescaled functions $\mathcal{T}(l)$, $\mathcal{D}(l)$, and $\mathcal{K}(l)$ are the solution of

$$\mathcal{T}(l)=\exp\left[-\int_0^l\left[2-\frac{1}{\nu[u(s)]}\right]ds\right]\ , \qquad (2.11)$$

$$\mathcal{D}(l)=\exp\left[\int_0^l\eta[u(s)]ds\right]\ , \qquad (2.12)$$

$$\mathcal{K}(l)=\int_0^l B[u(s)]\mathcal{T}^2(s)e^{(4-d)s}ds\ . \qquad (2.13)$$

Equation (2.7) relates the free energy of a system with cutoff Λ to another system with cutoff Λe^{-l}, with the form of the function unchanged. Thus, the system can be rescaled in space provided that the variables t and M are rescaled to new values. For the particular $\beta(u)$ functions that are of interest to critical phenomena, $u(l)$ approaches, as $l\rightarrow\infty$, a fixed-point value $u^*=\lim_{l\rightarrow\infty}u(l)$ determined by the condition

$$\beta(u^*)=0\ . \qquad (2.14)$$

The critical exponents α, β, γ, δ, ν, and η, with $\gamma=\beta(\delta-1)=(2-\eta)\nu$ and $d\nu=2-\alpha=2\beta+\gamma$, that characterize the asymptotic behavior of the thermodynamic properties and the correlation function near the critical point,[2] are related to the values of the functions $\nu(u)$ and $\eta(u)$ at the fixed point $u=u^*$,

$$\nu=\nu(u^*),\quad \eta=\eta(u^*)\ , \qquad (2.15)$$

while the exponent $\omega\equiv\omega_1$ of the first correction-to-scaling term in (1.2) is given by

$$\omega=\Delta/\nu=d\beta(u)/du\quad \text{at } u=u^*\ . \qquad (2.16)$$

The quantity on the left-hand side of (2.7) is the actual free energy of a system. Hence, it does not depend on the value of the parameter l on the right-hand side. Since l is arbitrary, it is possible to choose a special value $l=l^*$, called the match-point value,[30,50] such that the right-hand side assumes a form convenient for constructing a crossover free energy. The free-energy expression can be separated into a mean-field part $\Delta\tilde{A}_{\mathrm{MF}}$ and a fluctuation part $\Delta\tilde{A}_{\mathrm{fluct}}$,

$$\Delta\tilde{A}_s=\Delta\tilde{A}_{\mathrm{MF}}+\Delta\tilde{A}_{\mathrm{fluct}}(\kappa/\Lambda,M/\Lambda^{d/2-1},u)\ , \tag{2.17}$$

where κ is the mass term given by

$$\kappa^2=t+\tfrac{1}{2}u\Lambda^{4-d}M^2\ . \tag{2.18}$$

When (2.17) is used for the rescaled $\Delta\tilde{A}_s$ on the right-hand side of (2.7), both $\Delta\tilde{A}_{\mathrm{MF}}$ and $\Delta\tilde{A}_{\mathrm{fluct}}$ will contain the rescaling parameter l. If the match-point value $l=l^*$ is chosen such that

$$\Delta\tilde{A}_{\mathrm{fluct}}(l^*)=0\ , \tag{2.19}$$

then only the mean-field or classical free energy is left on the right-hand side of (2.17). It is for this classical free energy that we want to study the crossover behavior. Condition (2.19) yields a parameter value l^* which is no longer arbitrary but which is a function of t, M, and the coupling constant u. For this particular matching (2.7) becomes

$$\begin{aligned}\Delta\tilde{A}_s(t,M,u,\Lambda)\\ &=\Delta\tilde{A}_{\mathrm{MF}}(t\mathcal{T}(l^*),M\mathcal{D}^{1/2}(l^*),u(l^*),\Lambda e^{-l^*})\\ &\quad-\tfrac{1}{2}t^2\mathcal{K}(l^*)\ .\end{aligned} \tag{2.20}$$

The mean-field functional $\Delta\tilde{A}_{\mathrm{MF}}$ has a Landau expansion of the form

$$\Delta\tilde{A}_{\mathrm{MF}}(t,M,u,\Lambda)=\tfrac{1}{2}tM^2+\frac{1}{4!}u\Lambda^{4-d}M^4+\cdots\ . \tag{2.21}$$

We note that in (2.20) the variable t is proportional to $T-T_c$, while in (2.21) t is proportional to $T-T_c'$, where T_c' is the critical temperature implied by the classical equation; T_c' differs from the actual critical temperature T_c as further discussed in Sec. III C. The crossover mass term κ^2 becomes

$$\kappa^2=t\mathcal{T}(l^*)+\tfrac{1}{2}u(l^*)\Lambda(l^*)\mathcal{D}(l^*)M^2\ . \tag{2.22}$$

The solution of the match-point condition (2.19) becomes simple if we restrict ourselves to the critical isochore $M=0$. From (2.17) we see that in that case the match point is related to the root x_0 of the equation $\Delta\tilde{A}_{\mathrm{fluct}}(x_0,0,u(l^*))=0$ by

$$\kappa(l^*)=\Lambda e^{-l^*}x_0(u(l^*))\ . \tag{2.23}$$

The match-point condition (2.19) becomes harder to solve when $M\neq 0$. The solution has been determined by Nicoll and Albright in the ϵ expansion.[13]

III. PROPOSED CROSSOVER PROCEDURE

A. Formulation of crossover procedure

In order to implement the crossover theory outlined in Sec. II in practice, we introduce a number of approximations. We shall then provide evidence in support of these approximations.

The functions that appear in the renormalization-group equation (2.5) have been evaluated by Nicoll and Albright in terms of the ϵ expansion.[13] Schloms and Dohm have subsequently obtained expressions for these functions in three dimensions with the method of Borel resummation, but their results pertain to a different renormalization scheme.[39–41]

The function $\beta(u(l))$ in (2.9) has a nonzero fixed point u^* satisfying $\beta(u^*)=0$ in accordance with (2.14) and a Gaussian-like fixed point at $u=0$. Furthermore, in accordance with (2.16) the slope of the function $\beta(u)$ near $u=u^*$ equals the first correction-to-scaling exponent $\omega=\Delta/\nu$, the value of which is known.[51] A simple closed-form approximant satisfying these conditions is

$$\beta(u)=-\omega u+\frac{\omega}{u^*}u^2\ . \tag{3.1}$$

If this expression is substituted into (2.9) we obtain

$$u(l)=u^*+(u-u^*)Y\ , \tag{3.2}$$

with

$$Y=\frac{1}{1+\bar{u}(e^{\omega l}-1)} \tag{3.3}$$

and

$$u(l)\Lambda(l)=u^*\Lambda\mathcal{U}(l) \tag{3.5}$$

From (3.2) and (3.3) it follows that

$$u(l)\Lambda(l)=u^*\Lambda\mathcal{U}(l) \tag{3.5}$$

with

$$\mathcal{U}(l)=\bar{u}^{\,1/\omega}Y^{1/\omega}[1-(1-\bar{u})Y]^{(\omega-1)/\omega}\ . \tag{3.6}$$

For the function $\nu(u)$ we know that $\nu(u^*)=\nu$ in accordance with (2.15) and that $2-\nu^{-1}(u)$ is proportional to u to lowest order in perturbation theory. We thus propose

$$2-\nu^{-1}(u)\simeq(2-\nu^{-1})\bar{u}\ . \tag{3.7}$$

Substitution of (3.7) into (2.11) yields

$$\mathcal{T}(l)=Y^{(2-\nu^{-1})/\omega}\ . \tag{3.8}$$

The function $\eta(u)$ reduces to the exponent η at $u=u^*$ in accordance with (2.15). We therefore consider

$$\eta(u)=\eta\bar{u}^{\,2}\ . \tag{3.9}$$

The functional forms (3.1), (3.7), and (3.9) for the renormalization functions are fully consistent with the ϵ-expansion results to appropriate orders.[13] However, by adopting the actual theoretical critical-exponent values, we obtain closed-form approximants for these functions whose validity extends beyond that of a perturbation theory.

We note that Schloms and Dohm[41] have proposed a closed-form approximant for the function $\beta(u)$ which has a slightly more complicated structure than the approximation (3.1). Our function $\beta(u)$ cannot be identified directly with that of Schloms and Dohm, since they are based on two different renormalization schemes. Our results are obtained from a renormalization scheme in which the renormalization constants [i.e., the Z_i factors in (2.3)] are determined via renormalization conditions,[43,47,48] while Schloms and Dohm have employed the minimal subtraction scheme.[43,52,53] However, the differences in the two renormalization schemes are contained in the fixed-point value u^*. When we rewrite the function β as a function of the scaled variable $\bar{u}=u/u^*$, we find that the numerical values implied by our $\beta(\bar{u})$ are very close to the values implied by the function $\beta(\bar{u})$ of Schloms and Dohm for the values of u of interest in this paper. Furthermore, our approximants (3.7) and (3.9) for $2-\nu^{-1}(u)$ and $\eta(u)$, which are already written as a function of $\bar{u}$, turn out to be identical to approximants proposed by Schloms and Dohm.[41] Substitution of (3.9) into (2.12) yields

$$\mathcal{D}(l)=Y^{-\eta/\omega}e^{\eta(1-\bar{u})(Y-1)/\omega} . \tag{3.10}$$

This function is important for the crossover behavior of the order-parameter correlation function.[54] However, for the thermodynamic properties we prefer to simplify (3.10) as

$$\mathcal{D}(l)=Y^{-\eta/\omega} . \tag{3.11}$$

Strictly speaking, (3.11) is equivalent to replacing (3.9) with $\eta(u)=\eta\bar{u}$, which is only correct for u close to u^*. While this replacement does not affect the asymptotic power-law behavior it does affect the amplitudes of the correction-to-scaling contributions by terms of order η. We justify this approximation on the basis that the exponent η is small for three-dimensional systems.

Finally, to obtain an expression for $\mathcal{K}(l)$ we note that the function $B(u(l))$ in (2.13) originated from the additive renormalization of the specific heat and has an expansion of the form[43]

$$B(u)=1+O(u^2) . \tag{3.12}$$

Here we approximate $B(u)$ by unity, since the corrections are of the order of u^2 or η, which is small.[13,43] If we then substitute (3.8) into (2.13), the resulting integral cannot be evaluated analytically. However, if only the leading scaling and correction-to-scaling terms are treated exactly, we obtain

$$\mathcal{K}(l)=K_0(Y^{-\alpha/\Delta}-1)+\Delta\mathcal{K} , \tag{3.13}$$

where the constant K_0, given by

$$K_0=\frac{\nu}{\alpha\bar{u}^{\,1/\omega}\Lambda} \tag{3.14}$$

is related to the two-scale-factor amplitude ratio.[22,55,56] The correction $\Delta\mathcal{K}$ in (3.13) is only important for the Wegner correction terms, and for the leading correction to scaling term we find $\Delta\mathcal{K}=0.065(1-\bar{u})K_0Y^{1-\alpha/\Delta}$ which has a small coefficient as compared to the other terms. We adopt in practice

$$\mathcal{K}(l)=K_0(Y^{-\alpha/\Delta}-1) . \tag{3.15}$$

The match-point value l^*, determined by (2.23), was derived for $M=0$, but we shall use this expression for $M\neq 0$ as well. Moreover, we assume that the $u(l^*)$ dependence of x_0 is treated as a constant which can be absorbed by a redefinition of the cutoff wave number Λ:

$$e^{-l^*}=\kappa(l^*)/\Lambda . \tag{3.16}$$

This match-point value l^* needs to be substituted into the expressions (3.6), (3.8), (3.11), and (3.15) for $\mathcal{U}(l)$, $\mathcal{T}(l)$, $\mathcal{D}(l)$, and $\mathcal{K}(l)$ through the crossover function Y, given by (3.3), which becomes

$$Y=\frac{1}{1+\bar{u}[(\Lambda/\kappa)^{\omega}-1]} . \tag{3.17}$$

This crossover function can also be written in the form

$$Y=\frac{1}{\bar{u}(\Lambda/\kappa)^{\omega}}\,\frac{1}{1+[(1-\bar{u})/\bar{u}](\kappa/\Lambda)^{\omega}} . \tag{3.18}$$

The factor $\bar{u}(\Lambda/\kappa)^{\omega}$ in (3.18) reproduces the asymptotic singular critical behavior of the Helmholtz free energy and the remaining factor represents a "resummed" Wegner series in this approximation. If we expand this second factor in a series for small $(\kappa/\Lambda)^{\omega}$, we see that the coefficient $1-\bar{u}$ characterizes the rate of convergence of the Wegner series.

The functional form (3.17) for Y is by itself not sufficient to produce a complete crossover to the classical behavior of the free energy far away from the critical point. The reason is that in the derivation of the renormalization equation (2.5) terms like t/Λ^2 have been neglected and these terms do contribute in the classical region. Hence, to obtain a correct classical limit it is necessary to consider more explicitly the consequences of the existence of a finite cutoff Λ for the critical fluctuations. Nicoll and Bhattacharjee have investigated the effects of different froms of the cutoff in the case of the spherical model which they were able to analyze exactly.[30] They showed that for the spherical model the classical limit is recovered not as the limit $\Lambda/\kappa\rightarrow 1$, as suggested by (3.17), but instead as the limit $\Lambda/\kappa\rightarrow 0$. We assume that the cutoff effects for Ising-like systems yield the same feature which can be implemented by modifying the expression (3.17) for the crossover function Y to become[22]

$$Y=\frac{1}{1+\bar{u}[(1+\Lambda^2/\kappa^2)^{\omega/2}-1]} . \tag{3.19}$$

It is this additional feature to account for cutoff effects which distinguishes our procedure from the major results of Bagnuls and co-workers[31–34] and of Dohm and co-workers.[35–41] It is this feature which will enable us for fluids to represent thermodynamic-property data all the way to the classical region away from the critical point.[57]

The quantity κ is essentially an approximation for the inverse correlation length and the ratio κ/Λ is a measure of the distance from the critical point. We note that the crossover function Y depends on κ which itself depends on Y through (2.22). In practice, therefore, the crossover function Y is determined by a numerical iteration procedure for a given t and M. For the critical exponents and the fixed-point value u^* we adopt the values

$$\begin{aligned}&\nu=0.630\ \ (\alpha=3\nu-2=0.110) ,\\&\eta=0.0333 ,\\&\omega\nu=\Delta=0.51 ,\end{aligned} \tag{3.20}$$

in good agreement with the theoretical predictions for three-dimensional Ising-like systems.[31,51,58,59] As mentioned earlier, the fixed-point value u^* depends on the renormalization scheme. Here we use the value[33,51]

$$u^* = 0.472 \tag{3.21}$$

which, together with the expressions adopted for $\beta(u)$, $\nu(u)$, and $\eta(u)$, reproduces the correct universal ratios of the amplitudes of the asymptotic power laws as discussed below.

In conclusion our crossover procedure starts from a classical Helmholtz free energy A_{MF} which has an expansion of the form (2.21)

$$\Delta \tilde{A}_{\mathrm{MF}}(T,M;u\Lambda) = \tfrac{1}{2}tM^2 + \frac{1}{4!}u\Lambda M^4 + \cdots , \tag{3.22}$$

which is a function of t and M and which depends parametrically on the coefficient $u\Lambda$ of the M^4 term. The crossover Helmholtz free energy $\Delta\tilde{A}_s$ is then

$$\Delta \tilde{A}_s(t,M;u\Lambda) = \Delta \tilde{A}_{\mathrm{MF}}(t\mathcal{T}, M\mathcal{D}^{1/2}; u^*\Lambda\mathcal{U}) - \tfrac{1}{2}t^2\mathcal{K} \tag{3.23}$$

with $\mathcal{T}$, $\mathcal{D}$, $\mathcal{U}$, and $\mathcal{K}$ given by (3.8), (3.11), (3.6), and (3.15), while the crossover function Y is represented by (3.19). This common function Y depends on κ given by

$$\kappa^2 = t\mathcal{T} + \tfrac{1}{2}u^*\mathcal{U}\mathcal{D}M^2 . \tag{3.24}$$

The quantity κ serves as a measure of the distance from the critical point. At the critical isochore κ^{-1} becomes asymptotically proportional to the correlation length except for terms of the order of the exponent $\eta \simeq 0.03$.

B. Limiting behavior near the critical point

In our crossover model the critical region corresponds to $\Lambda/\kappa \gg 1$. In developing this model we have made a number of approximations. Hence we need to check how well our crossover procedure reproduces the known asymptotic behavior of the thermodynamic properties. This asymptotic behavior is characterized by power laws which represent the asymptotic behavior of various properties along specific paths such as the critical isochore $M=0$, the critical isotherm $t=0$, and the phase boundary below the critical temperature. The power laws for the reduced specific heat $\Delta\tilde{C}_v \propto (\partial^2\Delta\tilde{A}/\partial t^2)_M$, the reduced susceptibility $\tilde{\chi} \propto 1/(\partial^2\Delta\tilde{A}/\partial M^2)_t$, the reduced order parameter M_{cxc} along the phase boundary, the reduced ordering field $h = (\partial\Delta\tilde{A}/\partial M)_t$ along the critical isotherm, and the correlation length ξ along the critical isochore are summarized in Table I. The amplitudes of these power laws satisfy universal ratios which have been calculated theoretically. The power-law amplitudes implied by our crossover formalism can be readily obtained by expanding (3.23) around the critical point.

TABLE I. Asymptotic power laws.

Asymptotic power laws	
$\Delta\tilde{C}_v = \dfrac{A^+}{\alpha}(t)^{-\alpha}[1 + A_1^+(t)^{\Delta} + \cdots]$	$(M=0,\ t \geq 0)$
$\Delta\tilde{C}_v = \dfrac{A^-}{\alpha}\lvert t\rvert^{-\alpha}(1 + A_1^-\lvert t\rvert^{\Delta} + \cdots)$	$(M=0,\ t \leq 0)$
$M_{\mathrm{cxc}} = \pm B\lvert t\rvert^{\beta}(1 + B_1\lvert t\rvert^{\Delta} + \cdots)$	$(M = M_{\mathrm{cxc}},\ t \leq 0)$
$\tilde{\chi} = \Gamma^+(t)^{-\gamma}[1 + \Gamma_1^+(t)^{\Delta} + \cdots]$	$(M=0,\ t \geq 0)$
$\tilde{\chi} = \Gamma^-\lvert t\rvert^{-\gamma}(1 + \Gamma_1^-\lvert t\rvert^{\Delta} + \cdots)$	$(M = M_{\mathrm{cxc}},\ t \leq 0)$
$h = \pm D\lvert M\rvert^{\delta}(1 + D_1\lvert M\rvert^{\Delta/\beta} + \cdots)$	$(t=0)$
$\xi = \xi^+(t)^{-\nu}(1 + \xi_1^+\lvert t\rvert^{\Delta} + \cdots)$	$(M=0,\ t \geq 0)$

In Table II we give the asymptotic amplitude ratios implied by our crossover model together with theoretical values reported in the literature from the ϵ expansion,[13,60] from field-theoretical calculations[34] for $d=3$ and from a recent numerical analysis of the series expansions for the three-dimensional Ising model.[59] Identifying κ^{-1} with the correlation length ξ we find with the aid of (3.14) for our crossover model a value $R_\xi^+ = 0.28$ for the two-scale-factor amplitude ratio relating the amplitude ξ^+ to the amplitude $(A^+)^{1/d}$ to be compared with the value 0.27±0.01 predicted for this ratio.[61] In Table III we give also the ratios for the amplitudes of the Wegner correction terms. From the information in Tables II and III we conclude that our crossover model incorporates a satisfactory representation of the scaling behavior near the critical point. It is worth emphasizing that the small deviations of the amplitude ratios from the theoretically predicted values are consequences of the approximations we have made in formulating a *practical* and *simple* crossover procedure. They are not a consequence of the crossover theory itself which is capable of reproducing the theoretical amplitude ratios exactly.[13]

TABLE II. Asymptotic amplitude ratios.

	Γ^+/Γ^-	A^+/A^-	$A^+\Gamma^+/B^2$	$\Gamma^+ D B^{\delta-1}$
This model	4.96	0.50	0.052	1.72
ϵ expansion	4.9[a]	0.52±0.01[b]	0.048[a]	1.67[a]
$d=3$ field theory[c]	4.77±0.30	0.541±0.014	0.0594±0.0011	
Ising model[d]	4.95±0.15	0.523±0.009	0.058±0.001	

[a] Reference 13.
[b] Reference 60.
[c] Reference 34.
[d] Reference 59.

TABLE III. Amplitude ratios for the first Wegner correction term.

	A_1^+/B_1	B_1/Γ_1^+	ξ_1^+/A_1^+
This model	1.2	0.61	0.59
Theory	1.10±0.25[a]	0.90±0.21[a]	0.6±0.1[b]

[a] Reference 32.

[b] Reference 4.

C. Classical limit

In our crossover model the classical region far away from the critical point corresponds to the region where $\Lambda/\kappa \ll 1$. In the limit $\Lambda/\kappa=0$, we obtain $Y=1$, so that the functions $\mathcal{T}$ and $\mathcal{D}$ become equal to unity, while $\mathcal{H}$ becomes zero and we recover from (3.23) the classical expression for the Helmholtz free energy. However, what is of practical interest is the actual classical region where Λ/κ is small but not zero. To see what happens we expand the crossover function Y for small values of Λ/κ:

$$Y=1-\tfrac{1}{2}\bar{u}\omega\frac{\Lambda^2}{\kappa^2}+O\left[\frac{\Lambda^4}{\kappa^4}\right] . \tag{3.25}$$

Let us consider the critical isochore $M=0$. In first approximation $\kappa^2=t$ and

$$Y=1-\tfrac{1}{2}\bar{u}\omega\Lambda^2\frac{1}{t}+O\left[\frac{1}{t^2}\right] . \tag{3.26}$$

When equation-of-state data are fitted to a classical equation to determine the critical parameters, it is found that the critical parameters differ from the actual values. In particular the classical critical temperature is somewhat higher than the true critical temperature.[24] This shift is due to the neglect of the long-range fluctuations in the classical equation. This shift in the critical temperature occurs naturally in our crossover model. From (3.23) we note that the combination $t\mathcal{T}$ appears as the reduced temperature in the classical equation. From (3.8) and (3.26) we thus have in the classical region

$$t\mathcal{T}\equiv t'=t-\frac{1}{2}\left[2-\frac{1}{\nu}\right]\bar{u}\Lambda^2 . \tag{3.27}$$

Hence

$$\delta t_c=\frac{1}{2}\left[2-\frac{1}{\nu}\right]\bar{u}\Lambda^2 \tag{3.28}$$

is an apparent shift in the critical temperature.

We note in passing that it is also possible to estimate the critical-temperature shift δT_c from perturbation field theory directly. Up to one-loop order this theory yields[57]

$$\delta t_c \simeq \tfrac{1}{2}\bar{u}u^*\Lambda^2+O(u^2) . \tag{3.29}$$

This shift is of the same order of magnitude as that implied by (3.28).

IV. APPLICATION TO FLUIDS

To apply the crossover model derived from field theory we need to identify the order parameter M and the fields h and t appropriate for fluids. This identification is commonly made on the basis of the analogy between Ising model and lattice gas.[9,44,62] Let ρ be the density, T the temperature, μ the chemical potential and A/V the Helmholtz free energy per unit volume. These properties are made dimensionless[4] with the aid of the critical density ρ_c, the critical temperature T_c, and the critical pressure P_c:

$$\tilde{\rho}=\frac{\rho}{\rho_c},\quad \tilde{T}=-\frac{T_c}{T},\quad \tilde{\mu}=\frac{\mu\rho_c T_c}{P_c T},\quad \tilde{A}=\frac{AT_c}{VP_cT} . \tag{4.1}$$

In addition we define

$$\Delta\tilde{T}=\tilde{T}+1 , \tag{4.2}$$

$$\Delta\tilde{\mu}=\tilde{\mu}-\tilde{\mu}_0(\tilde{T}) , \tag{4.3}$$

$$\tilde{A}=\tilde{\rho}\,\tilde{\mu}_0(\tilde{T})+\tilde{A}_0(\tilde{T})+\Delta\tilde{A} , \tag{4.4}$$

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

Asymptotically close to the critical point the order parameter, for example, should be proportional to the density difference $\tilde{\rho}-1$, so that $M=c_\rho(\tilde{\rho}-1)$, $t=c_t\Delta\tilde{T}$, and $h\equiv(\partial\Delta\tilde{A}/\partial M)_t=c_\rho^{-1}\Delta\tilde{\mu}$, where c_ρ and c_t are system-dependent scale factors. However, a complication arises since the Helmholtz free energy of fluids is not a symmetric function of the order parameter unlike the field-theoretical model considered in Secs. II and III. The consequences of the presence of odd terms in the LGW Hamiltonian (2.2) have been analyzed by Nicoll.[44] A major consequence of the asymmetric terms is that they lead to a mixing of the field variables. Retaining mixing to linear order only, we make the identification[44,57]

$$M=c_\rho\Delta\tilde{\rho}+c\left[\frac{\partial\Delta\tilde{A}_s}{\partial t}\right]_M , \tag{4.5}$$

$$t=c_t\Delta\tilde{T}+c\left[\frac{\partial\Delta\tilde{A}_s}{\partial M}\right]_t , \tag{4.6}$$

with

$$\Delta\tilde{\rho}=\tilde{\rho}-1-d_1\Delta\tilde{T} . \tag{4.7}$$

Here c is a coefficient which determines the strength of the mixing, while the coefficient d_1 in (4.7) represents a global asymmetry. The corresponding expression for the critical part $\Delta\tilde{A}$ of the Helmholtz free energy $\tilde{A}$ becomes

$$\Delta\tilde{A}=\Delta\tilde{A}_s-c\left[\frac{\partial\Delta\tilde{A}_s}{\partial M}\right]_t\left[\frac{\partial\Delta\tilde{A}_s}{\partial t}\right]_M , \tag{4.8}$$

where $\Delta\tilde{A}_s$ Is the symmetric fluctuation-induced part of the Helmholtz free energy as given by (3.23). Equations (4.5)–(4.8), together with (3.23), specify the crossover model as we shall apply it to fluids.

We should note that this procedure introduces a number of approximations. The coefficients c_ρ, c_t, c, and d_1 are in principle (analytic) functions of temperature and density. We have no *a priori* knowledge of these coefficients since that would require the solution of the full exact renormalization-group equation for an actual fluid Hamiltonian. Here we treat these coefficients as adjustable constants. The transformation of variables as defined by (4.5) and (4.6), together with (4.7), has some important consequences for the temperature dependence of the diameter of the coexisting densities. First, mixing of the variables[63] causes the diameter of the coexistence curve to vary asymptotically as $|\Delta\tilde{T}|^{1-\alpha}$. Furthermore, for $Y=1$ it follows from (3.22) and (4.5) that $\Delta\tilde{\rho}$ has an expansion of the form $\Delta\tilde{\rho}=c_\rho^{-1}M-\frac{1}{2}cc_\rho^{-1}M^2+\cdots$. In the classical limit the order parameter at the phase boundary will vary as $M_{cxc}=\pm(6t/u\Lambda)^{1/2}+\cdots$. Hence, in the classical limit the coexistence curve diameter will not only contain $d_1\Delta\tilde{T}$ from (4.7), but also a term $\frac{1}{2}cc_\rho^{-1}M_{cxc}^2\simeq 3cc_\rho^{-1}(c_t/u\Lambda)\Delta\tilde{T}$. Thus, the coefficient d_1 in (4.7) cannot be identified with the slope of the classical coexistence-curve diameter. Instead this slope is the combined effect of d_1 and a contribution from the mixing.

As discussed by Nicoll,[44] terms of order ϕ^5 in the LGW Hamiltonian (2.2) not only lead to mixing of the field variables but also causes a new confluent singularity in the expansion (1.2) of $\Delta\tilde{A}$ with a new correction to scaling exponent Δ_5. The crossover of this additional confluent singularity to regular behavior can also be incorporated[22,23,44,64] and will be further discussed in a subsequent publication. In this paper we shall limit ourselves to an analysis of the crossover behavior as found from the ϕ^4-field theory for the first two terms of the expansion (3.22) of the classical Helmholtz free energy density.

The two important parameters of interest are the crossover parameters $\bar{u}$ and Λ. The parameter $\bar{u}$ is related to the rate of convergence of the Wegner expansion as discussed in Sec. III A; hence, it is a measure of the range of validity of the asymptotic critical power laws. The parameter Λ is a measure of the wave number where the fluctuations become microscopic; the field-theoretical parameter Λ can be related to the actual dimensional cutoff wave number q_D by writing

$$\Lambda=c_q q_D\ . \tag{4.9}$$

We estimate the coefficient c_q from the asymptotic relationship at the critical isochore between the variable κ and the inverse correlation length ξ^{-1}:

$$\kappa=c_q\xi^{-1}\ . \tag{4.10}$$

For $\kappa \ll 1$ at $M=0$, $\kappa^2\simeq tY^{(2-\nu^{-1})/\omega}$ and $Y\simeq\kappa^\omega/\bar{u}\Lambda^\omega$, so that

$$\kappa=(\bar{u}\Lambda^\omega)^{-(2\nu-1)/\omega}t^\nu\ . \tag{4.11}$$

Since the correlation ξ diverges as

$$\xi=\xi^+(\Delta\tilde{T})^{-\nu}\ , \tag{4.12}$$

and noting that $t=c_t\Delta\tilde{T}$ asymptotically, we obtain

$$c_q=c_t^\nu(\bar{u}\Lambda^\omega)^{-(2\nu-1)/\omega}\xi^+\ . \tag{4.13}$$

We emphasize that (4.13) with (4.9) are only meant to give a qualitative estimate of the physical cutoff wave number q_D. The cutoff q_D is a microscopic wave number that depends on the molecular nature of the fluid. In the field theory of critical phenomena the cutoff also depends on the manner in which the cutoff procedure is implemented. This variation is less important since the values of the cutoff in the different formulations should have the same order of magnitude. A specification of the precise physical meaning of q_D and its relationship to the molecular properties is outside the scope of the Landau-Ginzburg-Wilson-Hamiltonian approach and our approximation (3.19) does not originate from a specific cutoff procedure in perturbation theory. As we shall see in Sec. V, the value of q_D implied by (4.13) is indeed of microscopic order.

V. COMPARISON WITH EXPERIMENTAL DATA

A. Two-term Landau crossover model

To illustrate how the crossover procedure developed in the previous sections can be used to represent actual thermodynamic-property data of fluids we consider here the simplest possible classical equation, namely the Landau expansion (3.22) truncated after the first two terms:

$$\Delta\tilde{A}_{\mathrm{MF}}=\tfrac{1}{2}tM^2+\frac{u\Lambda}{4!}M^4\ . \tag{5.1}$$

Of course, a crossover model based on a two-term Landau expansion will not be able to represent the thermodynamic properties of fluids from the critical point all the way to the classical region, since more than two terms in the Landau expansion will be needed to reproduce the actual classical thermodynamic behavior far away from the critical point. However, a crossover model based on a two-term Landau expansion already contains the most important physical features of the crossover theory. Furthermore, even with a two-term Landau expansion we obtain a fundamental equation for the Helmholtz free energy for fluids in the critical region which improves upon the extended and revised parametric model used in our previous work.[4,15-18]

Our crossover model is determined by Eqs. (4.1)–(4.8) of Sec. IV with $\Delta\tilde{A}$ related to $\Delta\tilde{A}_s$ through (4.8). From (3.23) and (5.1) we conclude that $\Delta\tilde{A}_s$ is now given by

$$\Delta\tilde{A}_s=\tfrac{1}{2}t\mathcal{T}M^2\mathcal{D}+\frac{u^*\Lambda\mathcal{U}}{4!}M^4\mathcal{D}^2-\tfrac{1}{2}t^2\mathcal{K} \tag{5.2}$$

with the functions $\mathcal{T}$, $\mathcal{D}$, $\mathcal{U}$, and $\mathcal{K}$ given by (3.8), (3.11), (3.6), and (3.15):

$$\mathcal{T}=Y^{(2-\nu^{-1})/\omega}\ , \tag{5.3}$$

$$\mathcal{D}=Y^{-\eta/\omega}\ , \tag{5.4}$$

$$\mathcal{U}=\bar{u}^{\,1/\omega}Y^{1/\omega}[1-(1-\bar{u})Y]^{(\omega-1)/\omega}\ , \tag{5.5}$$

$$\mathcal{K} = \frac{\nu}{\alpha \bar{u}^{\,1/\omega}\Lambda}\left(Y^{-\alpha/\Delta}-1\right) . \tag{5.6}$$

The crossover function Y is given by (3.19)

$$Y = \frac{1}{1+\bar{u}[(1+\Lambda^2/\kappa^2)^{\omega/2}-1]} \tag{5.7}$$

with from (3.24)

$$\kappa^2 = t\mathcal{T} + \tfrac{1}{2}u^*\Lambda\mathcal{U}M^2\mathcal{D} . \tag{5.8}$$

The Helmholtz free-energy density $\tilde{A}$ is related to

$$\Delta\tilde{A} = \Delta\tilde{A}_s - c\left(\frac{\partial\Delta\tilde{A}_s}{\partial M}\right)_t \left(\frac{\partial\Delta\tilde{A}_s}{\partial t}\right)_M \tag{5.9}$$

by

$$\tilde{A} = \tilde{\rho}\tilde{\mu}_0(\tilde{T}) + \tilde{A}_0(\tilde{T}) + \Delta\tilde{A} . \tag{5.10}$$

To specify this Helmholtz free-energy density completely we represent the analytic background functions $\tilde{A}_0(\tilde{T})$ and $\tilde{\mu}_0(\tilde{T})$ by truncated Taylor expansions:

$$\tilde{A}_0(\tilde{T}) = -1 + \sum_{j=1}^{3} \tilde{A}_j(\Delta\tilde{T})^j , \tag{5.11}$$

$$\tilde{\mu}_0(\tilde{T}) = \sum_{j=0}^{4} \tilde{\mu}_j(\Delta\tilde{T})^j . \tag{5.12}$$

Equations (5.2)–(5.12), together with the definitions (4.5) and (4.6) of the variables M and t, specify our two-term Landau crossover model.

The crossover model has the following system-dependent constants: First it requires the critical parameters T_c, ρ_c and P_c; they are fixed at values deduced from an asymptotic analysis of experimental thermodynamic-property data close to the critical point. Secondly, it contains the crossover parameters $\bar{u}$ and Λ, the scaling-field parameters c_ρ, c_t, c, and d_1 and the background parameters $\tilde{A}_j$, which can be determined by fitting the crossover model to experimental P-ρ-T data. Finally, it contains the caloric background parameters $\tilde{\mu}_j$, which can be determined from experimental specific-heat or sound-velocity data as done previously in determining the same constants for the extended and revised parametric model.[16,18] Actually, for the calculation of caloric properties the coefficients $\tilde{\mu}_2$ and $\tilde{\mu}_3$ are only of interest; the coefficients $\tilde{\mu}_0$ and $\tilde{\mu}_1$ are related to the zero-point values of energy and entropy and are not considered here.

The relevant equations needed to calculate the various thermodynamic properties from our two-term Landau crossover model are presented in Appendixes A and B. The computation of the singular part $\Delta\tilde{A}$ of the Helmholtz free-energy density for a given density ρ and temperature T proceeds as follows.

(1) Calculate zeroth-order estimates for the variables t and M as $t_0 = c_t\Delta\tilde{T}$ and $M_0 = c_\rho\Delta\tilde{\rho}$, respectively.

(2) Calculate the corresponding values $Y_0 = Y(t_0, M_0)$ and $\kappa_0 = \kappa(t_0, M_0)$ from (5.7) and (5.8) by iteration.

(3) Calculate $(\partial\Delta\tilde{A}_s/\partial t)_M$ and $(\partial\Delta\tilde{A}_s/\partial M)_t$ in this approximation and obtain new estimates t_1 and M_1 for t and M from (4.5) and (4.6).

(4) Iterate the procedure until convergence is obtained.

B. Application to carbon dioxide

In a previous publication we have presented an extended and revised parametric equation of state for carbon dioxide in the critical region.[18] The constants in this equation of state were determined from a comparison with the experimental P-ρ-T data of Michels and co-workers[65,66] and with new specific-heat data of Edwards and Buckingham.[67] We have used the same experimental data to evaluate the two-term Landau crossover model formulated in this paper. The values of the coefficients for CO_2 in this model are presented in Table IV. In terms of a distance function $\tilde{R}$ defined as

$$\tilde{R} = \left(\frac{\partial^2\Delta\tilde{A}}{\partial M^2}\right)_t , \tag{5.13}$$

which is closely related to the symmetrized compressibility $\tilde{\chi} = (\partial\tilde{\rho}/\partial\tilde{\mu})_T$, the two-term Landau crossover equation is found to reproduce the experimental data within the estimated experimental accuracy in a region around the critical point bounded by

$$\tilde{R} \le 0.10 . \tag{5.14a}$$

This condition corresponds to a temperature range

$$298\ \mathrm{K} \le T \le 323\ \mathrm{K} \quad \text{at } \rho = \rho_c \tag{5.14b}$$

and a density range

$$245\ \mathrm{kg/m^2} \le \rho \le 600\ \mathrm{kg/m^3} \quad \text{at } T = T_c . \tag{5.14c}$$

With only two terms retained in the classical expansion the range of applicability of the crossover model is comparable to that of the parametric model used previously except that our new model does much better below the critical temperature, where the range of validity of the parametric model[18] is restricted to temperatures above 301.15 K. Furthermore, with the crossover model the deviations from the experimental data increase less rapidly when extrapolated outside the range of validity (5.14a).

The critical parameters were kept fixed at the values determined previously.[18] The crossover parameters $\bar{u}$ and Λ, the scaling-field parameters c_t, c_ρ, and c, and the equation-of-state background parameters d_1 and $\tilde{A}_j$ were determined from a fit to the experimental P-ρ-T data of Michels and co-workers[65,66] after a temperature correction of -0.035 K had been applied[18] to convert the experimental temperatures to the International Practical Temperature Scale (IPTS 68). With $\sigma_p = 0.0001$ MPa, $\sigma_T = 0.005$ K, and $\sigma_\rho = 0.01\%$ as the estimated errors in pressure, temperature, and density, the equation reproduces the experimental P-ρ-T data with a reduced χ^2 of 2.3. In Fig. 1 we present a comparison between these experimental pressure data and the calculated pressures. For most of the data the relative deviations from the equation are less than 0.03% with an average relative error of 0.01%. We also note that the deviations are distributed uniformly in the range of validity of the equation.

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

	Carbon dioxide	Steam	Ethylene
Critical-point parameters (fixed)			
T_c (K)	304.107	647.067	283.3401
ρ_c	467.69 kg/m^3	322.778 kg/m^3	7.623 mol/dm^3
P_c (MPa)	7.3916	22.0460	5.0397
Crossover parameters			
$\bar{u}$	0.559 50	0.565 75	0.447 27
Λ	1.3432	2.4806	2.1210
Scaling field parameters			
c_t	2.1479	2.9759	1.9863
c_ρ	2.3515	2.0490	2.4118
c	$-0.074\,858$	$-0.126\,00$	$-0.060\,476$
Equation of state background parameters			
d_1	$-0.702\,12$	$-0.334\,56$	$-0.464\,66$
$\tilde{A}_1$	-6.0225	-6.8552	-5.3401
$\tilde{A}_2$	$+9.5321$	$+5.2887$	$+5.3107$
$\tilde{A}_3$	-15.273	$+1.8933$	$+3.2807$
Caloric background parameters			
$\tilde{\mu}_2$	-18.445	-20.566	-13.636
$\tilde{\mu}_3$	$+3.1833$	$+14.844$	-13.174
$\tilde{\mu}_4$	$+19.81$	0 (fixed)	0 (fixed)
q_D^{-1} (Å)	2.0	1.0	1.4

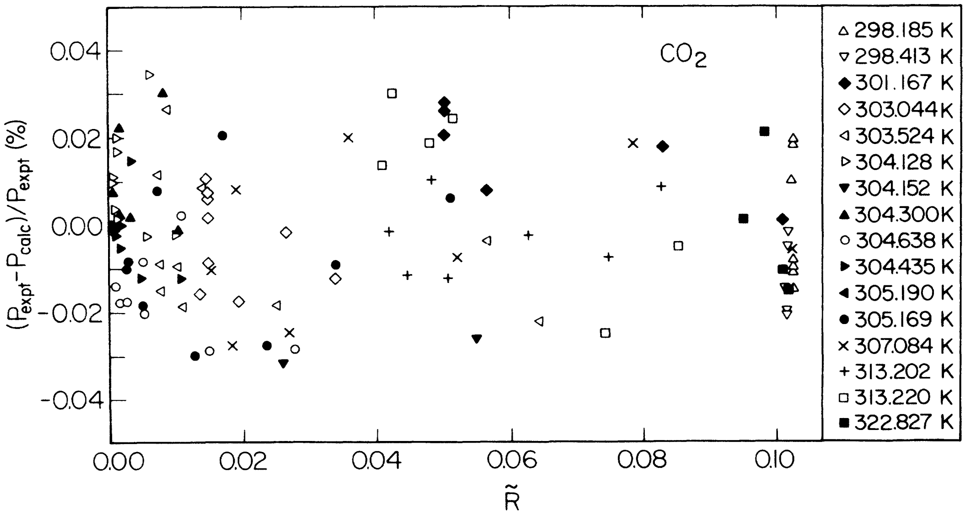

FIG. 1. Percentage differences between the experimental pressures obtained by Michels and co-workers (Refs. 65 and 66) for carbon dioxide in the critical region and the values calculated from our two-term crossover model. The deviations are plotted as a function of the distance variable $\tilde{R}$ defined by (5.13).

A crucial test of a thermodynamic surface in the critical region is its ability to represent the behavior of the isochoric specific heat C_v. In Fig. 2 we present a comparison of our equation with the experimental C_v data of Edwards and Buckingham[67] subsequently corrected for a revised estimate of the heat capacity of the empty calorimeter.[18] In this comparison $\tilde{\mu}_2$, $\tilde{\mu}_3$, and $\tilde{\mu}_4$ were treated as adjustable parameters for the background behavior of the specific heat. The equation reproduces these C_v data with an average absolute deviation of about ±2.3 J/(mol K) or an average relative deviation of about 1.5%.

The value found for the dimensionless cutoff Λ is 1.34. Since ξ^+ is 1.5 Å for carbon dioxide,[68] it follows from (4.9) and (4.13) that $q_D^{-1}=2.0$ Å which is indeed a microscopic distance. However, we found that the parameters $\bar{u}$ and Λ are highly correlated in practice. The reason is that close to the critical point the thermodynamic properties depend on $\bar{u}$ and Λ through $\bar{u}\Lambda^{\omega}$. To determine $\bar{u}$ and Λ as two separate independent parameters it will be necessary to compare with experimental data over a larger range of temperatures and densities by retaining higher-order terms in the Landau expansion (5.1).

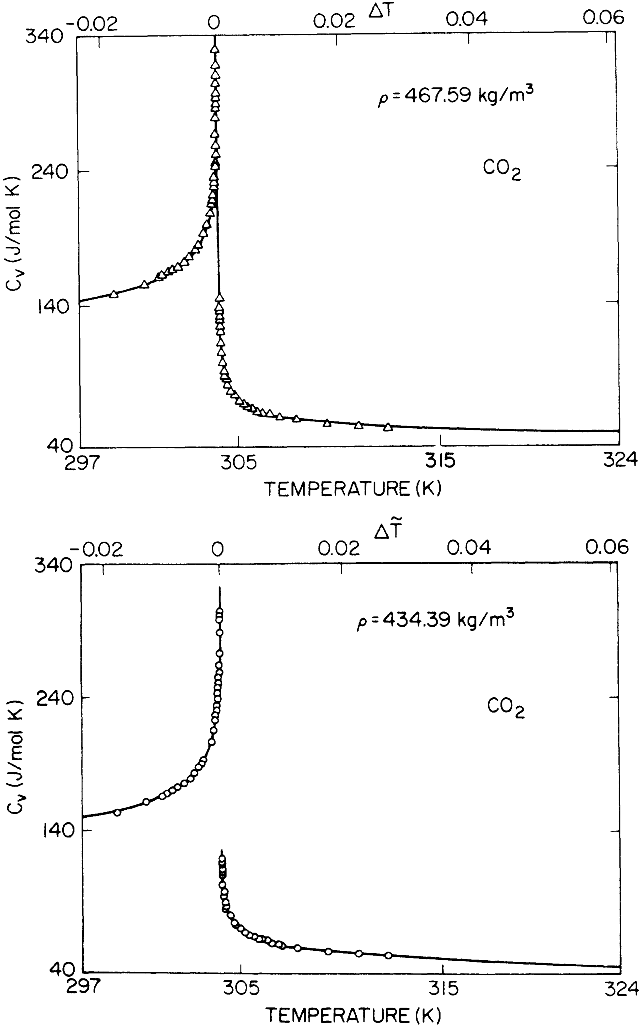

FIG. 2. The isochoric specific heat C_v of carbon dioxide in the critical region. The data points indicate the experimental data obtained by Edwards and Buckingham[67] and the solid curves represent the values calculated from our two-term crossover model.

C. Application to steam

As a second example we consider steam for which excellent thermodynamic-property data in the critical region are available.[16] An interesting feature of steam is that it has a much larger vapor-liquid asymmetry than most other simple fluids.

The values of the coefficients for H_2O are also presented in Table IV. The range of validity of our two-term crossover model is determined by

$$\tilde{R} \le 0.11 \ , \tag{5.15a}$$

which for steam corresponds to a temperature range

$$640 \text{ K} \le T \le 685 \text{ K} \quad \text{at } \rho=\rho_c \ , \tag{5.15b}$$

and a density range

$$195 \text{ kg/m}^3 \le \rho \le 500 \text{ kg/m}^3 \quad \text{at } T=T_c \ . \tag{5.15c}$$

The range (5.15a) is similar to the range (5.14a) found for carbon dioxide.

The critical parameters were kept fixed at the values previously determined by Levelt Sengers *et al.*[16] The crossover parameters $\bar{u}$ and Λ, the scaling-field parameters c_t, c_ρ, and c, and the equation-of-state background parameters d_1 and $\tilde{A}_j$ were determined from a fit to the experimental P-ρ-T data of Rivkin and co-workers[69,70] with the temperatures converted from IPTS 48 to IPTS 68. With $\sigma_p=0.001$ MPa, $\sigma_T=0.02$ K, and $\sigma_\rho=0.05\%$ as the estimated errors in pressure, temperature, and density, the equation reproduces the experimental P-ρ-T data with a reduced χ^2 of 1.1. A plot of the deviations of the experimental pressures from the calculated pressures is presented in Fig. 3 With $\xi^+=1.3$ Å for steam,[71] we find $q_D^{-1}=1.0$ Å.

We have also made a comparison of the equation with several experimental caloric properties of steam. With the system-dependent parameters deduced from the P-ρ-T data and with only two background coefficients $\tilde{\mu}_2$ and $\tilde{\mu}_3$ as adjustable parameters we show in Fig. 4 a comparison with speed-of-sound data obtained by Erokhin and Kalyanov.[72,73] In this comparison a difference of 0.06 K with the temperature scale of Rivkin *et al.* was assumed for reasons discussed in previous publications.[16,74] In Fig. 5 we show a comparison of the two-term crossover model with C_v data obtained by Baehr and Schomäcker.[75] The original experimental data were obtained by measuring the energy increments U_2-U_1 corresponding to temperature increments T_2-T_1 of the order of one degree. The solid curves in Fig. 5 represent the calculated values of $\bar{C}_v \equiv (U_2-U_1)/(T_2-T_1)$. In Fig. 6 we show a comparison with the C_p data obtained by Sirota and Maltsev[76] after applying temperature corrections recommended by Sirota, Maltsev, and Belyakova.[77] The data were actually obtained as enthalpy

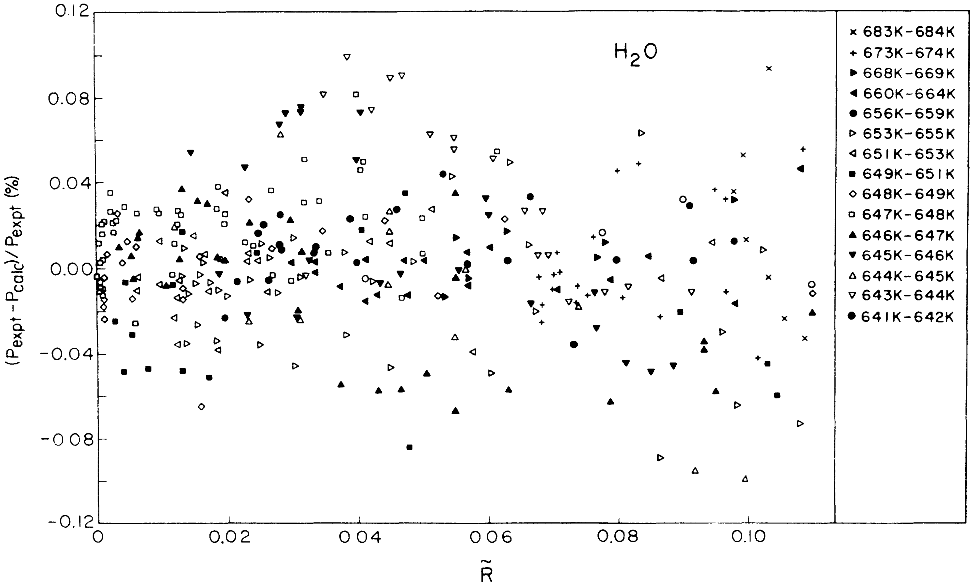

FIG. 3. Percentage differences between the experimental pressures obtained by Rivkin and co-workers (Refs. 69 and 70) for steam in the critical region and the values calculated from our two-term crossover model. The deviations are plotted as a function of the distance variable $\tilde{R}$ defined by (5.13).

increments H_2-H_1 corresponding to temperature increments T_2-T_1. The solid curves in Fig. 6 represent the calculated values of $\bar{C}_p \equiv (H_2-H_1)/(T_2-T_1)$. We emphasize that the comparisons in Figs. 5 and 6 were obtained without any adjustable parameters whatsoever. The agreement with the caloric data is within experimental accuracy.

D. Application to ethylene

As a third example we consider ethylene. Specifically we consider the P-ρ-T data reported by Hastings, Levelt Sengers, and Balfour[78] which have previously been compared with the extended and revised parametric model.[79,80] Our two-term crossover model represents the experimental P-ρ-T data in the range for which

$$\tilde{R} \leq 0.15\ , \qquad (5.16a)$$

which corresponds approximately to a temperature range

$$273\ \mathrm{K} \leq T \leq 303\ \mathrm{K} \quad \text{at } \rho=\rho_c\ , \qquad (5.16b)$$

and a density range

$$5.2\ \mathrm{mol/dm^3} \leq \rho \leq 10.7\ \mathrm{mol/dm^3} \quad \text{at } T-T_c\ . \qquad (5.16c)$$

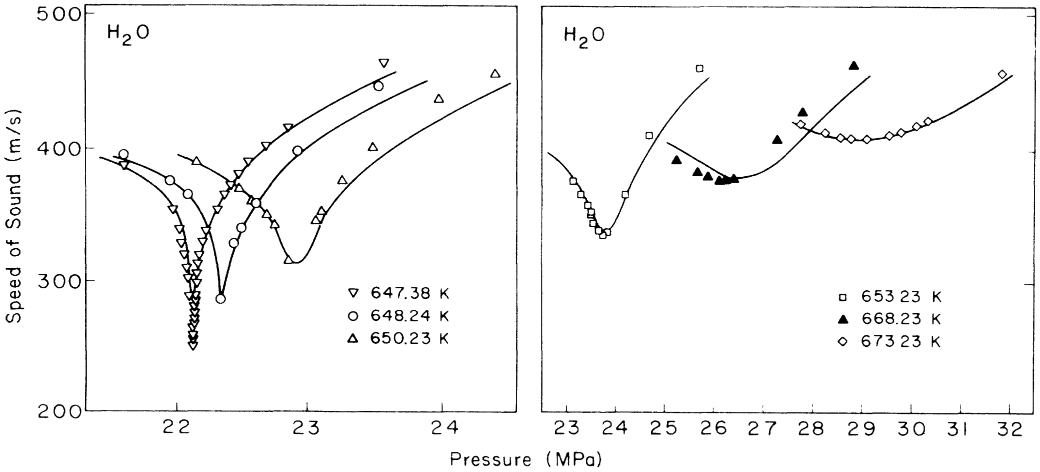

FIG. 4. The thermodynamic sound velocity of steam in the critical region. The data points indicate the experimental values obtained by Erokhin and Kalyanov (Refs. 72 and 73) and the solid curves represent the values calculated from our two-term crossover model.

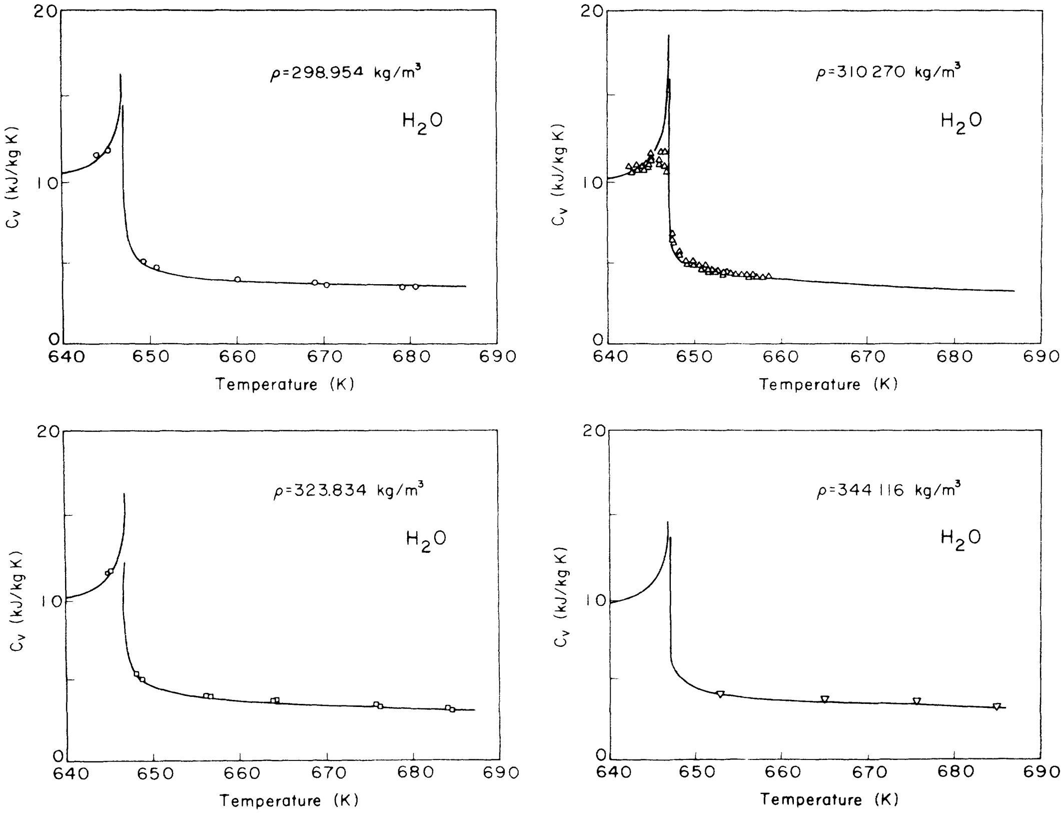

FIG. 5. The isochoric specific heat C_v of steam in the critical region. The data points indicate the experimental data obtained by Baehr and Schomäcker (Ref. 75) and the solid curves represent the values calculated from our two-term crossover model.

A plot of the deviations of the experimental pressures from the calculated pressures is presented in Fig. 7. The data obtained by Hastings, Levelt Sengers, and Balfour include some data in the metastable and precondensation region which were not included in the fit. With $\sigma_p = 3\times10^{-5}$ MPa, $\sigma_\rho = 3\times10^{-3}$ mol/dm^3, and $\sigma_T = 5\times10^{-4}$ K, the equation represents the P-ρ-T data with a reduced χ^2 of 3.8, which is of the same order as when the data are fitted to the revised and extended parametric equation.[79] However, we have adjusted the critical temperature slightly; the new value of T_c is within the range observed by Moldover.[81] With $\xi^+ = 1.8$ Å for ethylene,[71] we find $q_D^{-1} = 1.4$ Å.

With the equation of state parameters determined from the experimental P-ρ-T data and the caloric background parameters $\tilde{\mu}_2$ and $\tilde{\mu}_3$ as adjustable constants we can also make a comparison with the experimental speed-of-sound data obtained by Gammon for ethylene[82] as shown in Fig. 8. Again this property is satisfactorily represented by our crossover model.

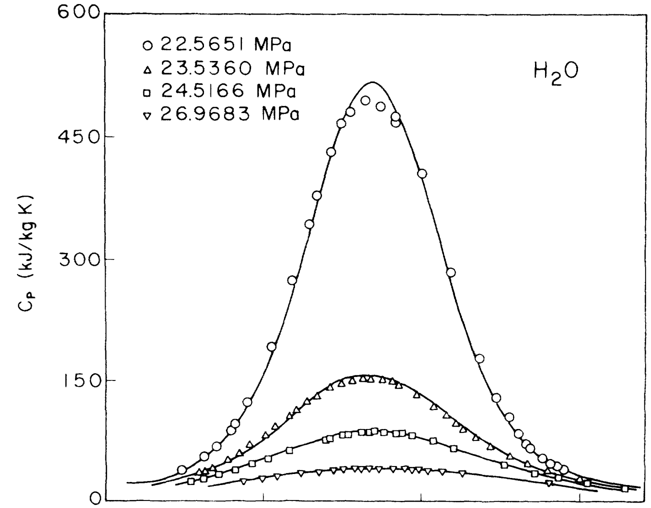

FIG. 6. The isobaric specific heat C_p of steam in the critical region. The data points indicate the experimental data obtained by Sirota and co-workers (Refs. 76 and 77) and the solid curves represent the values calculated from our two-term crossover model.

VI. CONCLUSION

In this paper we have presented a procedure for constructing a Helmholtz free-energy density which close to the critical point reproduces the correct asymptotic scal-

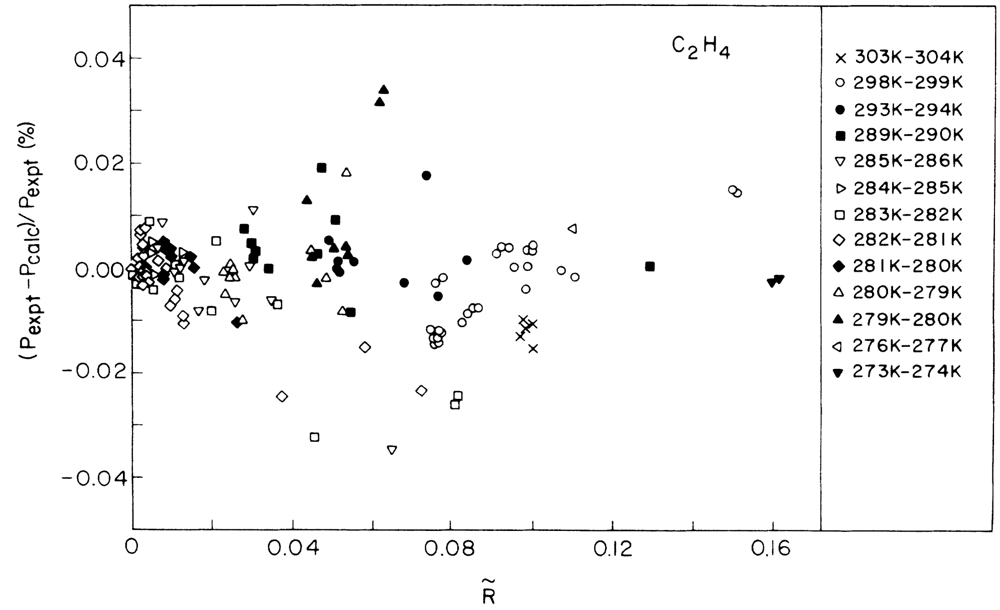

FIG. 7. Percentage differences between the experimental pressures obtained by Hastings, Levelt Sengers, and Balfour (Ref. 78) for ethylene in the critical region and the values calculated from our two-term crossover model. The deviations are plotted as a function of the distance parameter $\tilde{R}$ defined by (5.13).

ing and correction-to-scaling behavior and which far away from the critical point approaches a classical analytic equation. As an illustration how the procedure can be applied to actual thermodynamic-property data we have implemented the procedure for the simplest classical equation possible, namely a two-term Landau expansion. This procedure yields a fundamental equation which represents the thermodynamic behavior of fluids in a region around the critical point. In order to obtain a fundamental equation that will represent the thermodynamic behavior of fluids in the entire range of temperatures and densities where the effect of long-range critical fluctuations are observed, we need to apply the procedure to higher-order terms included in the classical Landau expansion. Such research is currently in progress. An alternative approach is to apply the procedure to a closed-form classical equation representing a summed classical Landau expansion.[23]

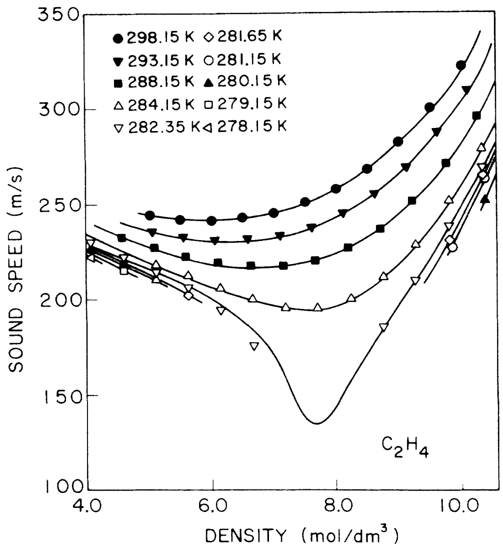

FIG. 8. The thermodynamic sound velocity of ethylene in the critical region. The data points indicate the experimental values obtained by Gammon (Ref. 82) and the solid curves represent the values calculated from our two-term crossover model.

The basic assumption in this work is that the effects of the critical fluctuations on the thermodynamic properties of actual fluids can be treated on the basis of a Landau-Ginzburg-Wilson Hamiltonian (2.2). This assumption implies that the leading confluent corrections to scaling are due to the ϕ^4 coupling. This assumption would break down if $u = u^*$; in that case the leading Wegner corrections would have zero amplitude and one would need the crossover behavior of higher-order terms in (2.2) explicitly as discussed by Bagnuls and co-workers.[33,34] In practice, though, we find $u < u^*$ for fluids. At a distance where the nonclassical effects of the higher-order terms might be important we expect that the system is well on its way to its crossover to the classical equation, so that an approximate treatment of the crossover behavior of these terms would be adequate. This expectation can only be confirmed *a posteriori* by a comparison with experimental data and it is consistent with the results obtained by Bagnuls, Bervillier, and Garrabos for xenon.[32]

ACKNOWLEDGMENTS

The authors have benefited from many stimulating discussions with J. F. Nicoll in the initial stage of this research. They also have received some valuable comments and suggestions from V. Dohm. The authors are indebted to A. Abbaci and S. Tang for their assistance in checking the equations of our crossover model. The research was supported by the Division of Chemical Sciences of the Office of Basic Energy Sciences of the Department of Energy under Grant No. DE-FG05-88ER13902.

APPENDIX A: THERMODYNAMIC RELATIONS

1. Reduced thermodynamic quantities

Here we list the reduced thermodynamic quantities:

$$\begin{gathered}\tilde{T}=-\frac{T_c}{T},\quad \tilde{\mu}=\frac{\mu\rho_c T_c}{TP_c},\quad \tilde{P}=\frac{PT_c}{TP_c}\,,\\ \tilde{\rho}=\frac{\rho}{\rho_c},\quad \tilde{A}=\frac{AT_c}{VTP_c},\quad \tilde{U}=\frac{U}{VP_c}\,,\\ \tilde{S}=\frac{ST_c}{VP_c},\quad \tilde{H}=\frac{HT_c}{VTP_c},\quad \tilde{\chi}=\left[\frac{\partial\tilde{\rho}}{\partial\tilde{\mu}}\right]_T,\\ \tilde{C}_v=\frac{C_v T_c}{VP_c},\quad \tilde{C}_p=\frac{C_p T_c}{VP_c},\quad \tilde{W}=W\left[\frac{\rho_c T_c}{P_c T}\right]^{1/2},\end{gathered}\tag{A1}$$

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

2. Fundamental equations

Here we list the fundamental equations:

$$\Delta\tilde{T}=\tilde{T}+1\,,\tag{A2}$$

$$\Delta\tilde{\rho}=\tilde{\rho}-1-d_1\Delta\tilde{T}\,,\tag{A3}$$

$$\tilde{A}=\tilde{\rho}\,\tilde{\mu}_0(\tilde{T})+\tilde{A}_0(\tilde{T})+\Delta\tilde{A}\,,\tag{A4}$$

with

$$\tilde{A}_0(\tilde{T})=-1+\tilde{A}_1\Delta\tilde{T}+\tilde{A}_2(\Delta\tilde{T})^2+\tilde{A}_3(\Delta\tilde{T})^3\,,\tag{A5}$$

$$\tilde{\mu}_0(\tilde{T})=\tilde{\mu}_0+\tilde{\mu}_1\Delta\tilde{T}+\tilde{\mu}_2(\Delta\tilde{T})^2+\tilde{\mu}_3(\Delta\tilde{T})^3+\mu_4(\Delta\tilde{T})^4\,.\tag{A6}$$

The term $\Delta\tilde{A}$ in (A4) is the crossover part of the free energy density as specified in Appendix B.

3. Derived thermodynamic quantities

Here we list the derived thermodynamic quantities:

$$\tilde{P}=\tilde{\rho}\tilde{\mu}-\tilde{A},\quad \tilde{\mu}=\Delta\tilde{\mu}+\tilde{\mu}_0(\tilde{T})\,,\tag{A7}$$

$$\Delta\tilde{\mu}=\left[\frac{\partial\Delta\tilde{A}}{\partial\Delta\tilde{\rho}}\right]_{\Delta\tilde{T}},\tag{A8}$$

$$\tilde{\chi}^{-1}=\left[\frac{\partial^2\Delta\tilde{A}}{\partial\Delta\tilde{\rho}^2}\right]_{\Delta\tilde{T}},\tag{A9}$$

$$\begin{aligned}\left[\frac{\partial\tilde{P}}{\partial\tilde{T}}\right]_{\tilde{\rho}}=&-\frac{d\tilde{A}_0(\tilde{T})}{d\tilde{T}}+\rho\frac{\partial^2\Delta\tilde{A}}{\partial\Delta\tilde{\rho}\,\partial\Delta\tilde{T}}-\frac{d_1}{\tilde{\chi}_T}\tilde{\rho}\\ &-\left[\frac{\partial\Delta\tilde{A}}{\partial\Delta\tilde{T}}\right]_{\Delta\tilde{\rho}}+d_1\Delta\tilde{\mu}\,,\end{aligned}\tag{A10}$$

$$\begin{aligned}\left[\frac{\partial^2\Delta\tilde{A}}{\partial\Delta\tilde{T}^2}\right]_{\tilde{\rho}}=&\left[\frac{\partial^2\Delta\tilde{A}}{\partial\Delta\tilde{T}^2}\right]_{\Delta\tilde{\rho}}-2d_1\frac{\partial^2\Delta\tilde{A}}{\partial\Delta\tilde{\rho}\,\partial\Delta\tilde{T}}\\ &+d_1\left[\frac{\partial^2\Delta\tilde{A}}{\partial\Delta\tilde{\rho}^2}\right]_{\Delta\tilde{T}},\end{aligned}\tag{A11}$$

$$\tilde{U}=-\frac{d\tilde{A}_0(\tilde{T})}{d\tilde{T}}-\tilde{\rho}\frac{d\tilde{\mu}_0(\tilde{T})}{d\tilde{T}}+d_1\Delta\mu-\left[\frac{\partial\Delta\tilde{A}}{\partial\Delta\tilde{T}}\right]_{\Delta\tilde{\rho}},\tag{A12}$$

$$\tilde{S}=-\tilde{A}-\tilde{T}\,\tilde{U}\,,\tag{A13}$$

$$\tilde{H}=\tilde{P}-\tilde{T}\,\tilde{U}\,,\tag{A14}$$

$$\tilde{C}_v/\tilde{T}^2=-\frac{d^2\tilde{A}_0(\tilde{T})}{d\tilde{T}^2}-\tilde{\rho}\frac{d^2\tilde{\mu}_0(\tilde{T})}{d\tilde{T}^2}-\left[\frac{\partial^2\Delta\tilde{A}}{\partial\Delta\tilde{T}^2}\right]_{\tilde{\rho}},\tag{A15}$$

$$\tilde{C}_p=\tilde{C}_v+\frac{\tilde{\chi}}{\tilde{\rho}^2}\left[\tilde{P}-\tilde{T}\left[\frac{\partial\tilde{P}}{\partial\tilde{T}}\right]_{\tilde{\rho}}\right]^2,\tag{A16}$$

$$\tilde{W}=\left[\frac{\tilde{\rho}}{\tilde{\chi}}\frac{\tilde{C}_p}{\tilde{C}_v}\right]^{1/2}.\tag{A17}$$

APPENDIX B: EQUATIONS FOR TWO-TERM LANDAU CROSSOVER MODEL

1. Fundamental equations

Here we list the fundamental equations:

$$t=c_t\Delta\tilde{T}+c\left[\frac{\partial\Delta\tilde{A}_s}{\partial M}\right]_t,\tag{B1}$$

$$M=c_\rho\Delta\tilde{\rho}+c\left[\frac{\partial\Delta\tilde{A}_s}{\partial t}\right]_M,\tag{B2}$$

$$\Delta\tilde{A}=\Delta\tilde{A}_s-c\left[\frac{\partial\Delta\tilde{A}_s}{\partial M}\right]_t\left[\frac{\partial\Delta\tilde{A}_s}{\partial t}\right]_M,\tag{B3}$$

$$\Delta\tilde{A}_s=\tfrac{1}{2}t\mathcal{T}M^2\mathcal{D}+\frac{u^*\Lambda\mathcal{U}}{4!}M^4\mathcal{D}^2-\tfrac{1}{2}t^2\mathcal{K}\,,\tag{B4}$$

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

$$\mathcal{D}=Y^{-\eta/\omega}\,,\tag{B6}$$

$$\mathcal{U}=\bar{u}^{\,1/\omega}Y^{1/\omega}[1-(1-\bar{u})Y]^{(\omega-1)/\omega}\,,\tag{B7}$$

$$\mathcal{K}=\frac{\nu}{\alpha\bar{u}^{\,1/\omega}\Lambda}(Y^{-\alpha/\Delta}-1)\,,\tag{B8}$$

$$Y=\frac{1}{1+\bar{u}[(1+\Lambda^2/\kappa^2)^{\omega/2}-1]}\,,\tag{B9}$$

$$\kappa^2=t\mathcal{T}+\tfrac{1}{2}u^*\Lambda\mathcal{U}M^2\mathcal{D}\,.\tag{B10}$$

2. Thermodynamic derivatives

Here we list the thermodynamic derivatives:

$$\left(\frac{\partial\Delta\tilde{A}}{\partial\Delta\tilde{T}}\right)_{\Delta\tilde{\rho}}=c_t\left(\frac{\partial\Delta\tilde{A}_s}{\partial t}\right)_M,\quad \left(\frac{\partial\Delta\tilde{A}}{\partial\Delta\tilde{\rho}}\right)_{\Delta\tilde{T}}=c_\rho\left(\frac{\partial\Delta\tilde{A}_s}{\partial M}\right)_t, \tag{B11}$$

$$\left(\frac{\partial^2\Delta\tilde{A}}{\partial\Delta\tilde{T}^2}\right)_{\Delta\tilde{\rho}}=c_t^2\left(\frac{\partial^2\Delta\tilde{A}_s}{\partial t^2}\right)_M G^{-1}, \tag{B12}$$

$$\frac{\partial^2\Delta\tilde{A}}{\partial\Delta\tilde{T}\,\partial\Delta\tilde{\rho}}=c_tc_\rho\left\{\frac{\partial^2\Delta\tilde{A}_s}{\partial t\,\partial M}-c\left[\left(\frac{\partial^2\Delta\tilde{A}_s}{\partial t\,\partial M}\right)^2-\left(\frac{\partial^2\Delta\tilde{A}_s}{\partial t^2}\right)_M\left(\frac{\partial^2\Delta\tilde{A}_s}{\partial M^2}\right)_t\right]\right\}G^{-1}, \tag{B13}$$

$$\left(\frac{\partial^2\Delta\tilde{A}}{\partial\Delta\tilde{\rho}^2}\right)_{\Delta\tilde{T}}=c_\rho^2\left(\frac{\partial^2\Delta\tilde{A}_s}{\partial M^2}\right)_t G^{-1}, \tag{B14}$$

with

$$G=\left(1-c\frac{\partial^2\Delta\tilde{A}_s}{\partial t\,\partial M}\right)^2-c^2\left(\frac{\partial^2\Delta\tilde{A}_s}{\partial t^2}\right)_M\left(\frac{\partial^2\Delta\tilde{A}_s}{\partial M^2}\right)_t . \tag{B15}$$

3. Derivatives of crossover function

Here we list the derivatives of the crossover function:

$$\left(\frac{\partial\kappa^2}{\partial t}\right)_M=F_1(t,M)\mathcal{T}, \tag{B16}$$

$$\left(\frac{\partial\kappa^2}{\partial M}\right)_t=F_1(t,M)u^*\Lambda M\mathcal{U}\mathcal{D}, \tag{B17}$$

$$\left(\frac{\partial Y}{\partial t}\right)_M=F_2(t,M)\mathcal{T}, \tag{B18}$$

$$\left(\frac{\partial Y}{\partial M}\right)_t=F_2(t,M)u^*\Lambda M\mathcal{U}\mathcal{D}, \tag{B19}$$

with

$$F_1=\frac{1}{1+f_1f_2}, \tag{B20}$$

$$F_2=f_1Y^2F_1, \tag{B21}$$

$$f_1=\frac{\bar{u}\Lambda^2\omega}{2\kappa^4}\left(1+\frac{\Lambda^2}{\kappa^2}\right)^{\omega/2-1}, \tag{B22}$$

$$\begin{aligned}f_2=&-\left(\frac{2-\nu^{-1}}{\omega}\right)t\mathcal{T}Y\\&-\tfrac{1}{2}u^*\Lambda M^2\mathcal{D}\mathcal{U}Y\left[\frac{1-\eta}{\omega}\right.\\&\left.-\left(\frac{\omega-1}{\omega}\right)\frac{(1-\bar{u})Y}{1-(1-\bar{u})Y}\right].\end{aligned} \tag{B23}$$

4. Universal constants

Here we list the universal constants:

$$\begin{aligned}&\nu=0.630,\\&\eta=0.0333,\\&\alpha=3\nu-2=0.110,\\&\Delta=0.51(\omega=\Delta/\nu=0.809\,52),\\&u^*=0.472.\end{aligned} \tag{B24}$$

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