PHYSICAL REVIEW B VOLUME 36, NUMBER 1 1 JULY 1987

Crossover from singular to regular thermodynamic behavior of fluids in the critical region

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(Received 5 March 1987)

A procedure is presented for constructing equations for the thermodynamic properties of fluids in the critical region which incorporates the crossover from Ising-like scaled behavior near the critical point to regular (i.e., classical) behavior away from the critical point in a theoretically consistent manner. When the procedure is applied to a truncated classical Landau expansion, we obtain an accurate representation of the thermodynamic properties of carbon dioxide in both the asymptotic critical region and in the crossover regime.

The thermodynamic behavior of systems near a critical point satisfies scaling laws with universal critical exponents and universal scaling functions. Fluids near the vapor-liquid critical point are expected to belong to the universality class of Ising-like systems, i.e., three-dimensional systems with short-range forces and a scalar order parameter.[1] Indeed, experimental thermodynamic-property data of fluids in the vicinity of the critical point can be represented accurately by scaled fundamental equations, extended to include leading correction-to-scaling terms and revised to partially account for vapor-liquid asymmetry.[2] However, the agreement with experimental data deteriorates very rapidly as soon as the scaled equations are extrapolated outside the near-critical region. The problem is that equations that only account for the asymptotic critical behavior do not extrapolate properly to any known limit away from the critical point, neither at low or high densities nor at low or high temperatures. Outside the critical region, the thermodynamic surface of fluids is well represented by classical equations that are analytic in temperature and density. Such analytic equations, however, fail to reproduce the correct singular thermodynamic behavior near the critical point.

The challenge is to develop a thermodynamic surface that not only incorporates the asymptotic critical behavior, but that also accounts for the crossover to the regular behavior further away from the critical point. A first attempt to address this problem phenomenologically was made by Chapela and Rowlinson.[3] They tried to represent the pressure as the sum of a scaled equation and an analytic equation with weights determined by a switch function. Unfortunately, use of any switch function for blending two thermodynamic equations leads to spurious behavior of the derivatives of the surface in the transition regime.[4] Another empirical method has been proposed by Fox, in which the crossover from a classical potential outside the critical region to a scaled potential near the critical point is accomplished by an appropriate redefinition of the variables in the classical potential.[5,6] While this procedure avoids the pitfalls of the switch-function approach, it still does not account for certain important features of the crossover phenomenon which are discussed below.

In the renormalization-group approach to critical phenomena[7] one takes into account the cooperative effect of fluctuations with all wave numbers up to a maximum value Λ, which corresponds to an inverse microscopic length. As emphasized elsewhere,[8] the critical region corresponds to $\xi\Lambda \gg 1$, where ξ is the correlation length of the order-parameter fluctuations; in this region the thermodynamic potential can be represented by a resummed Wegner expansion.[9-11] Crossover to a classical behavior will take place when $\xi\Lambda$ becomes of order unity.[12]

We have developed a procedure to construct fundamental equations for the thermodynamic properties of fluids that incorporate the crossover from the critical to the classical region. An earlier attempt to deduce the crossover behavior from the renormalization-group theory was made by Rudnick and Nelson.[13] Our procedure is based on the subsequent theoretical analysis of the crossover phenomenon made by Nicoll and co-workers[8,12,14-16] and has the following properties.

(a) Near the critical point we not only recover the asymptotic scaling laws but also obtain a realistic estimate for the leading Wegner correction terms. This is accomplished by including a resummed Wegner series as has also been done by Dohm[9] and by Bagnuls, Bervillier, Meiron, and Nickel.[11]

(b) Certain properties, like the specific heat C_v, contain both singular and regular terms produced by the critical fluctuations which merge and cancel in the classical region far away from the critical point. This nonscaling feature of the specific heat is included in the manner described by Nicoll and Albright.[8]

(c) Classical equations that represent data away from the critical point predict critical parameters, in particular a critical temperature, that differ from those of the actual critical point.[3] Our crossover formalism also accounts for this apparent shift in T_c, which is a consequence of the manner in which the cut-off parameter Λ appears in the crossover function.[16]

A derivation of our crossover formalism is documented in a thesis[17] and will be presented in a future publication. Here we specify the procedure and show how it can be used to make a comparison with experimental data. The temperature T, the mass density ρ, the Helmholtz-free-energy density A/V, and the chemical potential μ are made dimensionless[2] with the aid of the critical temperature T_c, pressure P_c, and density ρ_c: $\tilde{T}=-T_c/T$, $\tilde{\rho}=\rho/\rho_c$, $\tilde{A}=AT_c/VTP_c$, and $\tilde{\mu}=\mu\rho_c T_c/TP_c$. In addition, we define $\Delta\tilde{T}=\tilde{T}+1$ and $\Delta\tilde{\rho}=\tilde{\rho}-1$. The fundamental equation for the Helmholtz-free-energy density $\tilde{A}(\tilde{T},\tilde{\rho})$ is written in the form

$$\tilde{A}=\tilde{\rho}\tilde{\mu}_0(\tilde{T})+\tilde{A}_0(\tilde{T})+\Delta\tilde{A}\ , \tag{1}$$

where $\tilde{\mu}_0(\tilde{T})$ and $\tilde{A}_0(\tilde{T})$ are analytic functions representing background contributions and where $\Delta\tilde{A}$ incorporates the effect of critical fluctuations. Any classical equation (by definition) implies a Landau expansion for $\Delta\tilde{A}$ near the critical point of the form

$$\Delta\tilde{A}_{\mathrm{cl}}(t,m,u_0)=\tfrac{1}{2}tm^2+\frac{u_0}{4!}m^4+\cdots\ , \tag{2}$$

where $t=c_t\Delta\tilde{T}$ and $m=c_\rho\Delta\tilde{\rho}$, the coefficients c_t, c_ρ, and u_0 being system-dependent constants.

A fundamental equation that accounts for the crossover from the classical behavior to the critical behavior of a symmetric Ising model or lattice gas is then obtained by replacing $\Delta\tilde{A}$ in (1) with

$$\Delta\tilde{A}_s=\Delta\tilde{A}_{\mathrm{cl}}(tY^{(2-1/\nu)/\omega},mY^{-\eta/2\omega},u_0Y^{1/\omega})-\frac{\nu}{2\alpha\bar{u}\bar{\Lambda}}t^2(Y^{-\alpha/\Delta}-1)\ , \tag{3}$$

with

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

Here $\bar{u}=u_0/u^*\bar{\Lambda}$, where $u^*=0.472$ is the value of the fixed-point coupling constant,[18,19] while $\bar{\Lambda}$ is the cutoff, and $\bar{\kappa}$ the inverse correlation length in suitable dimensionless units. For the critical exponents we have adopted the values $\nu=0.630$, $\eta=0.033$, $\alpha=3\nu-2=0.110$, and $\omega\nu=\Delta=0.51$ in good agreement with the theoretical predictions for three-dimensional Ising-like systems.[2] The variable $\bar{\kappa}$ serves as a measure of the distance from the critical point which we in practice approximate by relating $\bar{\kappa}^2$ to the inverse compressibility

$$\bar{\kappa}^2=tY^{(2-1/\nu)/\omega}+\tfrac{1}{2}u_0m^2Y^{(1-\eta)/\omega}\ . \tag{5}$$

Equations (4) and (5) determine the crossover function Y as a function of t and m. In the limit $\bar{\kappa}/\bar{\Lambda}\to\infty$, Y approaches unity and we recover from (3) the classical equation. In the limit $\bar{\kappa}/\bar{\Lambda}\to 0$, Y becomes proportional to $(\bar{\kappa}/\bar{\Lambda})^\omega$ and we reproduce the singular asymptotic critical behavior with amplitude ratios $A_+/A_-=0.50$ for the specific heat above and below T_c, $\Gamma_+/\Gamma_-=4.96$ for the susceptibility above and below T_c, $A_+\Gamma_+/B^2=0.052$ for the relationship between A_+, Γ_+, and the amplitude B of the coexistence curve and $\Gamma_+DB^{\delta-1}=1.72$ for the relationship between Γ_+, B, and the amplitude D of the chemical potential along the critical isotherm; these values for the amplitude ratios are in good agreement with the theoretical predictions.[8,20-22] The behavior of the crossover function Y is governed by two parameters: the ratio $\bar{u}$ and the cutoff $\bar{\Lambda}$. The parameter $\bar{u}$ is related to the universal properties of the Wegner series, including its rate of convergence.[8] The parameter $\bar{\Lambda}$ determines the densities and temperatures where the transition from critical to classical behavior takes place. Our crossover function is chosen so that it reproduces the known crossover behavior in the limit $n\to\infty$, corresponding to the spherical model.[14]

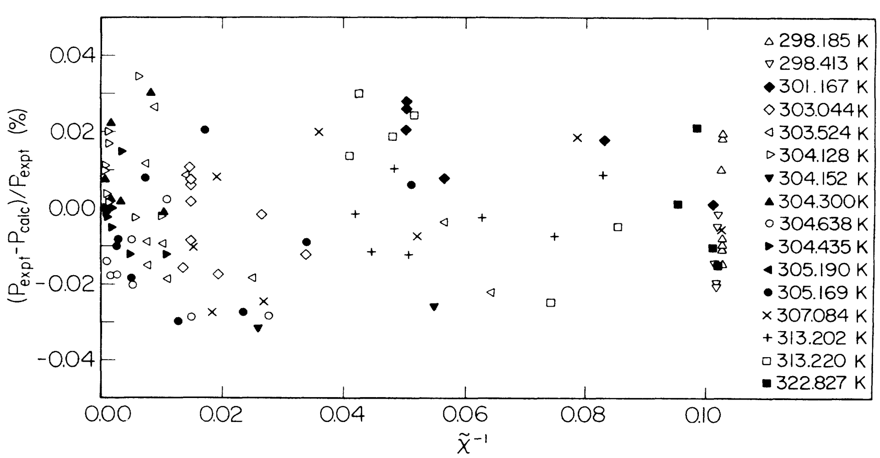

FIG. 1. Percentage differences between the experimental pressure data of Michels and co-workers (Refs. 23 and 24) for CO_2 in the critical region and the values calculated from our crossover model.

An actual fluid does not exhibit the vapor-liquid symmetry of the lattice gas; this asymmetry is reflected by a nonzero slope of the classical coexistence-curve diameter and by the presence of higher-order terms in the expansion (2) that are odd in the order parameter. There are two consequences of this lack of symmetry.[14] The first, called mixing, corresponds to a rotation of the thermodynamic axes. To linear order in the mixing parameter c, this effect can be incorporated by redefining the variables t and m through

$$t = c_t \Delta\tilde{T} + c\left(\frac{\partial \Delta\tilde{A}_s}{\partial m}\right)_t , \tag{6}$$

$$m = c_\rho(\Delta\tilde{\rho} - \tilde{D}_1 \Delta\tilde{T}) + c\left(\frac{\partial \Delta\tilde{A}_s}{\partial t}\right)_m , \tag{7}$$

and by evaluating $\Delta\tilde{A}$ in (1) as

$$\Delta\tilde{A} = \Delta\tilde{A}_s(t,m) - c\left(\frac{\partial \Delta\tilde{A}_s}{\partial m}\right)_t \left(\frac{\partial \Delta\tilde{A}_s}{\partial t}\right)_m . \tag{8}$$

The second consequence is that an m^5 term in the expansion (2) leads to further contributions to the crossover corresponding to a confluent singular behavior with a new critical exponent Δ_5; this feature can also be embodied in our procedure[16,17] but is here approximated by a contribution $\tilde{D}_1\Delta\tilde{T}$ to the coexistence-curve diameter.

To illustrate a practical application of our crossover treatment, we consider the simplest classical equation possible, which is obtained by retaining only the first two terms in the Landau expansion (2). If we approximate the functions $\tilde{\mu}_0(\tilde{T})$ and $\tilde{A}_0(\tilde{T})$ in (1) by truncated Taylor expansions

$$\tilde{\mu}_0(\tilde{T}) = \sum_{i=0}^{4} \tilde{\mu}_i (\Delta\tilde{T})^i , \tag{9}$$

$$\tilde{A}_0(\tilde{T}) = -1 + \sum_{i=1}^{3} \tilde{A}_i (\Delta\tilde{T})^i , \tag{10}$$

the equations in this Rapid Communication specify the Helmholtz free energy completely. We have made a comparison of this crossover model with experimental data for carbon dioxide. The best available experimental pressure data for CO_2 are still those of Michels and coworkers.[23,24] With only two terms in the Landau expansion (2), our crossover model represents these pressure data for $\tilde{\chi}^{-1} = (\partial\tilde{\mu}/\partial\tilde{\rho})_{\tilde{T}} \leq 0.11$; this range corresponds to temperatures from 298 to 322 K at $\rho = \rho_c$ and densities from 245 to 600 kg/m^3 at $T = 298$ K. A plot of the differences $\Delta = (P_{\text{expt}} - P_{\text{calc}})/P_{\text{expt}}$ between experimental and calculated pressures is shown in Fig. 1. These differences are of the order of the estimated experimental accuracy[25] and are uniformly distributed in the range of validity of the equation.

A crucial test of a nonclassical thermodynamic surface is its ability to represent the behavior of the specific heat C_v near the critical point. Recently, new accurate experimental data for the C_v of CO_2 in the critical region have been obtained by Edwards.[26] In Fig. 2 we present a comparison between our two-term crossover Landau model and the experimental data of Edwards which were obtained at two isochores corresponding to $\rho = 434.39$ kg/m^3 and $\rho = 467.59$ kg/m^3 and subsequently corrected for a revised estimate of the heat capacity of the empty calorimeter.[24] From Fig. 2 we see that our model indeed describes the crossover from the divergent behavior of the C_v at the

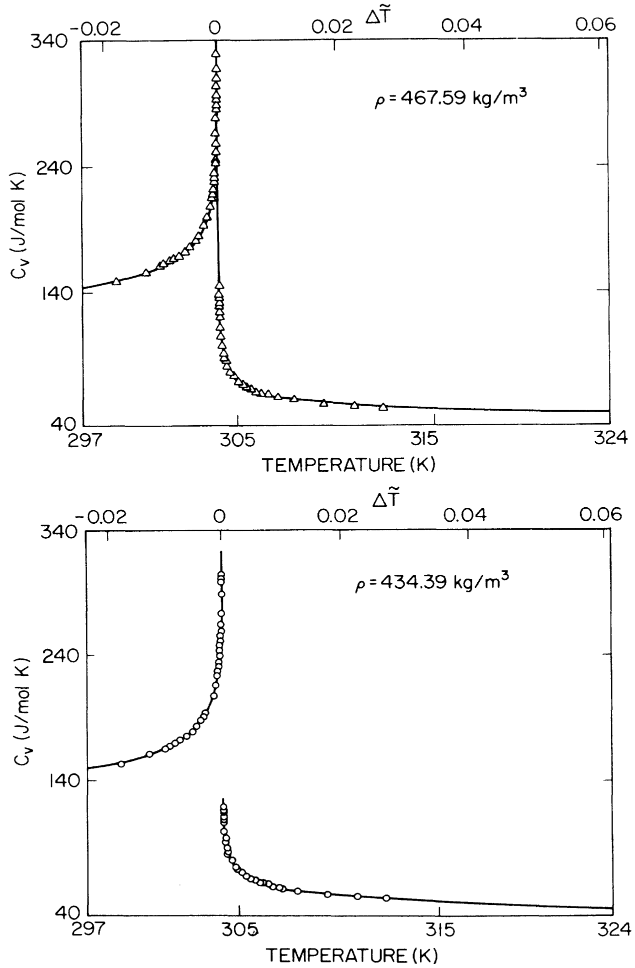

FIG. 2. Comparison of our crossover model with the new experimental C_v data of Edwards (Ref. 26) for CO_2.

TABLE I. Values of the system-dependent constants in our crossover model for CO_2.

Critical parameters:	$P_c = 7.3719$ MPa, $T_c = 304.107$ K, $\rho_c = 467.69$ kg/m^3
Scaling parameters:	$c_t = 2.0774$, $c_\rho = 2.2958$, $c = -0.040154$
Crossover parameters:	$\bar{u} = 0.94781$, $\bar{\Lambda} = 0.70437$
Background parameters:	$\tilde{D}_1 = -0.46810$, $\tilde{A}_1 = -6.0209$, $\tilde{A}_2 = 6.3611$, $\tilde{A}_3 = -20.25$, $\tilde{\mu}_2 = -16.445$, $\tilde{\mu}_3 = 4.9303$, $\tilde{\mu}_4 = 96.427$

critical point to the finite jump implied by the classical behavior away from the critical point.

The values of the system-dependent constants in our two-term Landau crossover model are presented in Table I. For the cut-off parameter we find $\bar{\Lambda}^{-1}=1.4197$; in dimensional units this corresponds to $\Lambda^{-1}=3.2$ Å, which is indeed a microscopic distance. The parameters $\tilde{\mu}_0$ and $\tilde{\mu}_1$ determine the zero-point values of enthalpy and entropy which are not of importance here.[25]

The range of validity of our crossover model can be further extended by including higher-order terms in the Landau expansion (2). However, with only two terms in the Landau expansion, the range is already sufficiently large to make contact with the region where practical engineering equations become applicable.

We are indebted to J. F. Nicoll for valuable discussions throughout this research, to T. J. Edwards for providing us with his experimental C_v data prior to publication, to J. M. H. Levelt Sengers for her stimulating interest and support, and to M. E. Fisher for a critical reading of the manuscript. The research at the University of Maryland was supported by the National Science Foundation under Grant No. DMR 82-05356.

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