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A Crossover Description for the Thermodynamic Properties of Fluids in the Critical Region[1]

P. C. Albright,[2] J. V. Sengers,[2,3] J. F. Nicoll,[4] and M. Ley-Koo[5]

We have developed a "crossover" formalism that reconciles the singular asymptotic critical behavior of the thermodynamic properties of fluids with the classical behavior of these properties well away from the critical point. The proposed formalism is based on theoretical predictions for the crossover behavior suggested by the renormalization-group theory of critical phenomena. We demonstrate the formalism for a fluid whose classical behavior away from the critical point is represented by the equation of state of van der Waals.

KEY WORDS: critical phenomena; equation of state; renormalization-group theory; specific heat; thermodynamic properties; van der Waals equation.

1. INTRODUCTION

There has always been an interest in the accurate description of the thermophysical properties of fluids. Much effort has been expended on the construction of equations of state; the simplest examples include the equations of van der Waals, Berthelot, and Dieterici [1]. These so-called classical equations all show the existence of a critical point; nevertheless, they do not predict the nonanalyticities that are seen in real systems [2]. The renormalization-group (RG) theory of Wilson [3], Fisher [4], and

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[2] Thermophysics Division, National Bureau of Standards, Gaithersburg, Maryland 20899, U.S.A.

[3] Institute for Physical Science and Technology, University of Maryland, College Park, Maryland 20742, U.S.A.

[4] Pangaro Incorporated, 800 Third Street NE, Washington, D.C. 20002, U.S.A.

[5] Facultad de Sciencias, Departamento de Fisica, Universidad Nacional Autónoma de Mexico, P.O. Box 21-939, 04000 Mexico, D.F., Mexico.

Wegner [5], on the other hand, does properly deal with the critical fluctuations and yields a description in terms of scaling laws in the vicinity of the critical point. Unfortunately, these scaling laws appear to be valid only in a region extremely close to the critical point, and they cannot be extrapolated away from it [6]. The goal of determining in a physically consistent manner a valid description for fluid systems legitimate near the critical point as well as away from it defines the crossover problem that is addressed in this paper.

2. CLASSICAL THEORY

The classical theories have as a common feature the analytic expansion of the free energy about the critical point into a Landau series [7]. For example, near the critical point the mean-field Gibbs free energy of a symmetric magnet may be written as

$$G_{\mathrm{MF}}(t, h, u; m) = \frac{1}{2} tm^2 + \frac{u}{4!} m^4 - hm \tag{1}$$

where t is proportional to the temperature difference $T - T_c$, h is the magnetic field, and m is the order parameter. In this example, m is the magnetization. In a fluid m is related to the density difference $\rho - \rho_c$, while h corresponds to the chemical potential difference $\mu - \mu(\rho_c, T)$. The coefficient u is a coupling constant characteristic of the system.

The mean-field theory yields a thermodynamic behavior near the critical point which is incompatible with experiment [2]. It should be emphasized, however, that away from the critical point the mean-field assumptions are plausible, and in fact classical equations do work outside the critical region.

3. ASYMPTOTIC CRITICAL BEHAVIOR

The asymptotic critical behavior of the thermodynamic properties can be described in terms of scaling laws initially developed phenomenologically by Widom [8]. The renormalization-group theory has yielded theoretical predictions for the scaling functions and critical exponents [9, 10]; the theory can be extended by the addition of Wegner correction-to-scaling terms [11]. In this form the theory has been quite successful in representing the thermodynamic properties of fluids in the critical region [12].

Nevertheless, this approach has a number of shortcomings. First, the scaled equations have a limited range of validity. Second, the RG theory reveals the presence of nonscaling features arising in properties such as the specific heat [13, 14]. The crossover theory presented here reduces to the Wegner series near the critical point and to the classical mean-field behavior away from the critical region. Furthermore, the nonscaling features mentioned above arise naturally within the theory.

4. THE CROSSOVER THEORY

The basic notion of Wilson's original formulation of the renormalization-group theory is that most fluctuations contribute to the critical behavior and must be accounted for. However, there are degrees of freedom that do not contribute. For example, we do not expect such things as the molecular shape and the extent of hydrogen bonding among molecules to affect the essential feature of the critical behavior (i.e., that the system is undergoing large-scale fluctuations). These short-wavelength features will affect the nonuniversal aspects such as the location of the critical point but do not couple with the rest of the fluctuations. Thus, we expect to be able to divide the modes of the system into those that are of a short range and a relatively high frequency, which are not strongly coupled, and those of a longer wavelength, which do couple strongly and hence lead to the essential (and universal) nonanalytic behavior near the critical point.

This implies, then, that there is a cutoff Λ in those wave numbers that must be considered when determining the fluctuation-dominated behavior of the system. The original technique proposed by Wilson was to rescale successively the lengths in the system in such a way that the correlation length ξ becomes of the order of the scale of the cutoff; the resultant theory (with now renormalized parameters) may then be dealt with classically. Within the RG theory this heuristic procedure has been carried out for the case of the symmetric magnet [15], as well as for asymmetric systems [16].

In these calculations it is initially desirable to ignore the nontrivial contributions from the cutoff. In the asymptotic critical region, of course, the dominant length scale is the correlation length, and thus the cutoff is unimportant except as a trivial measure of the length scale. In this region we therefore ignore contributions of order $1/(\xi\Lambda)^2$. However, in regions further away from the critical point, where $\xi\Lambda \sim 1$, these terms will not be trivial. A crossover theory which does not account for the transition to the region dominated by the cutoff must fail, since it represents only the summation of the Wegner series (i.e., a summation of those terms which are independent of the scale of the cutoff). The effect of ignoring the cutoff may be repaired, however, by requiring the crossover theory to agree in the appropriate limit with the exactly soluble spherical model [17, 18].

5. APPLICATION TO A VAN DER WAALS GAS

As stated in the Introduction, our goal is to model the crossover behavior in fluids. Although the theory alluded to above deals with the magnetic case, universality arguments enable us to use these results in fluids [2]. The analogy between the magnetic Ising model and the lattice gas suggests that the Gibbs free energy of a magnetic system, as a function of the temperature T and magnetic field, corresponds to the pressure P, taken as a function of the temperature T and chemical potential μ of the fluid [2]. More specifically, we take the potential $\tilde{P}=(P/T)(T_c/P_c)$ as a function of $t=(T-T_c)/T$ and $\Delta\tilde{\mu}=[\mu(\rho, T)-\mu_0(T)]$, where $\mu_0(T)$ is the classical form for the chemical potential at $\rho=\rho_c$ above T_c and its analytic continuation below T_c.

As an illustration we demonstrate the crossover methodology for a fluid whose classical behavior is represented by the van der Waals equation

$$P=\frac{T\rho}{1-b\rho}-a\rho^2 \tag{2}$$

where a and b are constants. As a first step we define the singular part $\tilde{P}_s$ of the potential by $-\tilde{P}_s \equiv -\tilde{P}+1+\Delta\tilde{\mu}+3t$ and derive from Eq. (2)

$$-\tilde{P}_s=\frac{8}{3}(1+\delta\rho)\ln\left[\frac{1+\delta\rho}{1-\frac{1}{2}\delta\rho}\right]-4\delta\rho-3(\delta\rho)^2+3t(\delta\rho)^2-\delta\rho\Delta\tilde{\mu} \tag{3}$$

where $\delta\rho=(\rho-\rho_c)/\rho_c$. In deducing Eq. (3), we identified the critical parameters P_c, T_c, and ρ_c with those implied by the van der Waals equation, Eq. (2). In practice, we use Eq. (3) in terms of the actual critical parameters, which differ from those implied by the classical equation. The crossover formalism presented here accounts for an apparent shift in the critical parameters from the values implied by a classical theory in its region of validity [18, 19].

Expanding Eq. (3) about the critical point, we find

$$-\tilde{P}_s\approx\frac{1}{2}t'm^2+\frac{u}{4!}m^4+\frac{uv}{5!}m^5-hm \tag{4}$$

where

$$v=-(u/9)^{1/4}, \qquad t'=6v^2t, \qquad m=-\delta\rho/v, \qquad h=-v\Delta\tilde{\mu} \tag{5}$$

This illustrates the reason for the definition of $\tilde{P}_s$; it is this part of the classical potential that contains the Landau series, Eq. (1). In this form we can substitute the results predicted by a RG analysis of the crossover behavior of the Landau series. Specifically, we find [18]

$$-\tilde{P}_s = \left\{\frac{4}{3}\left[(1+R\delta\rho)\ln\left(\frac{1+R\delta\rho}{1-\frac{1}{2}R\delta\rho}\right)+(1-R\delta\rho)\ln\left(\frac{1-R\delta\rho}{1+\frac{1}{2}R\delta\rho}\right)\right]\right.$$
$$\left.-3R^2(\delta\rho)^2+3t\mathscr{T}\mathscr{D}(\delta\rho)^2-\frac{1}{2}t^2K\right\}$$
$$+\mathscr{U}^{-1/4}\mathscr{V}\left\{\frac{4}{3}\left[(1+R\delta\rho)\ln\left(\frac{1+R\delta\rho}{1-\frac{1}{2}R\delta\rho}\right)\right.\right.$$
$$\left.\left.-(1-R\delta\rho)\ln\left(\frac{1-R\delta\rho}{1+\frac{1}{2}R\delta\rho}\right)\right]-4R\delta\rho\right\}$$
$$-\frac{2}{3}\bar{u}(t\Delta\tilde{\mu}\delta_{\mathrm{m}}+6t^2\delta\rho\delta_{\mathrm{h}})-\delta\rho\Delta\tilde{\mu} \quad (6)$$

where

$$\mathscr{T}=Y^{(2-1/\nu)/\omega},\qquad \mathscr{U}=Y^{1/\omega},\qquad \mathscr{D}=Y^{-\eta/\omega},$$
$$\mathscr{V}=Y^{(\Delta_5+\frac{1}{2}\eta\nu-\beta)/\Delta},\qquad R=\mathscr{U}^{\frac{1}{4}}\mathscr{D}^{\frac{1}{2}} \quad (7)$$

and

$$K=A_0\left[\frac{Y^{-\alpha/\Delta}-1}{\alpha/\Delta}+A_1(1-\bar{u})\frac{Y^{1-\alpha/\Delta}-1}{1-\alpha/\Delta}\right]$$
$$\delta_{\mathrm{m}}=E_1(Y^{e_1}-1)+E_2(Y^{e_1+1}-1) \quad (8)$$
$$\delta_{\mathrm{h}}=F_1(Y^{f_1}-1)+F_2(Y^{f_1+1}-1)$$

with $e_1=(\beta+\Delta_5-1)/\Delta$ and $f_1=(\Delta_5+\beta\delta-2)/\Delta$.

Here, α, β, δ, ν, and η are the usual Ising critical exponents that characterize the asymptotic behavior of the thermodynamic properties and the correlation function [2], $\Delta=\omega\nu\approx0.5$ is the first Wegner correction-to-scaling exponent, and $\Delta_5\approx1.2$ is the first asymmetric Wegner exponent [11, 20]. A_0, A_1, E_1, E_2, F_1, and F_2 are constants; the values of some of these are constrained by universal amplitude ratios [16, 18]. The function Y is a crossover function which is related to the inverse correlation length $\kappa=\xi^{-1}$ by

$$Y^{-1}=1+\bar{u}\left[\left(1+\frac{\Lambda^2}{\kappa^2}\right)^{\omega/2}-1\right] \quad (9)$$

The parameter κ is a measure of the distance from the critical point; in the limit $\kappa/\Lambda \to 0$ we recover the singular asymptotic critical behavior, while in the limit $\kappa/\Lambda \to \infty$ we recover the classical behavior.

The behavior of the crossover function, Eq. (9), is governed by the two parameters $\bar{u}$ and Λ; Λ is a measure of the cutoff wave number for the critical fluctuations, and $\bar{u} = u/u^*$, where u^* is the fixed-point value of the coupling constant [17]. These two parameters have distinct physical consequences. The constant $\bar{u}$ is related to the rate of convergence of the Wegner series [21]; when $\bar{u} = 1$, for example, there are no correction-to-scaling terms for a system described by Eq. (1), and thus such a system exhibits pure power-law behavior throughout the critical region. The parameter Λ, on the other hand, determines the region of validity of the critical (Wegner) theory; when $\kappa \sim \Lambda$ the correlation length is of the order of the cutoff, the system is no longer governed by strongly coupled fluctuations, and we expect classical behavior.

It should be noted that a pure fluid system does not exhibit the vapor–liquid symmetry of the lattice gas; this is reflected by the presence of the m^5 term in Eq. (4) as opposed to Eq. (1). A RG analysis [16] shows that there are two consequences of this lack of symmetry for the critical behavior. The first, called mixing, corresponds to a rotation of the thermodynamic axes in the temperature–chemical potential plane. For simplicity, we have here ignored this effect, noting that the associated coupling constant appears to be small [12]. The second consequence leads to a new correction-to-scaling term with exponent Δ_5 and, furthermore, has global consequences, since this effect is responsible for the linear coexistence-curve diameter in the classical limit [19]. We have therefore included this term in our crossover potential given by Eq. (6).

In order to specify the crossover potential given by Eq. (6) completely, we must determine the dependence of the distance parameter κ on the temperature and density. We find that as a first approximation [17, 18]

$$\kappa^2 = t\mathscr{T} + \frac{3}{4}\mathscr{U}\mathscr{D}(\delta\rho)^2 \tag{10}$$

which defines implicitly the crossover function Y given by Eq. (9).

In the potential given by Eq. (6), the functions K, δ_{m}, and δ_{h} embody the nonscaling behavior of the critical free energy [15, 17, 21]. Note that only in the limit $Y \to 1$ (i.e., the classical limit) is it possible to separate a genuine analytic background term $\propto t^2$ in the free energy from the analytic fluctuation-driven term $\propto t^2$ contributed by the nonscaling term K. An asymptotic (i.e., noncrossover) theory cannot resolve this ambiguity. The other nonscaling contributions, δ_{h} and δ_{m}, lead to similar effects.

The crossover potential presented in this section satisfies the following set of properties. First, the asymptotic critical behavior is reproduced in detail; the Wegner series is, to lowest order, completely contained in the crossover function. The effect of asymmetries is easily included; the theory is in full accord with the phenomenological scaling theory of Ley-Koo and Green [11]. Second, the nonscaling behavior necessary in interpreting, for example, specific heat experiments [13] is predicted. Third, the theory is fully consonant with RG results; predicted amplitude ratios, for example, are automatically contained in the potential given by Eq. (6) [15]. Approximations are controlled; it is possible to include higher-order effects in a straightforward manner [18]. Finally, the transition is made to the classical behavior in a physically intuitive manner; the phenomenology of the crossover, such as the shift in the apparent critical point, is replicated as well.

6. DISCUSSION

Using, then, Eqs. (6)–(10), we have generated an expression for the van der Waals fluid that will correctly reproduce the entire Wegner series in the critical region up to terms linear in the asymmetric coupling constant yet which makes the transition to the classical regime in a theoretically consistent manner. Using the simplest form for the crossover functions, we have plotted the behavior of various thermodynamic functions in Figs. 1–4 [18].

Figure 1 shows the behavior of the crossover function Y along the critical isochore for two values of $\bar{u}$; we have arbitrarily set $\Lambda^2 = 0.1$

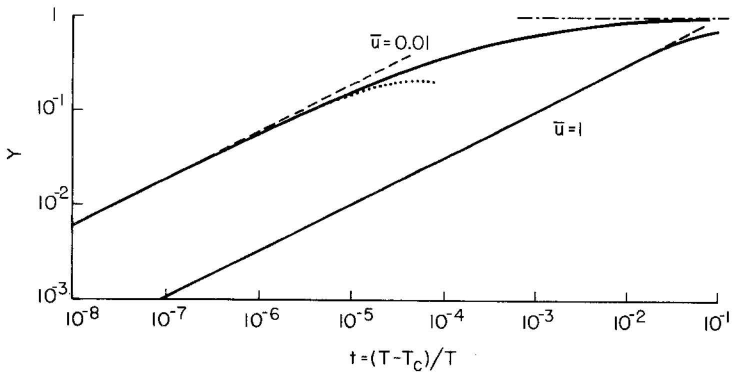

Fig. 1. Log–log plot of the crossover function Y vs reduced temperature $t > 0$ along the critical isochore, for two values of $\bar{u}$. Λ^2 is taken to be 0.1. The dashed line shows asymptotic power-law behavior; the dotted line, the effect of considering the first Wegner correction as well. Also shown is the limiting classical behavior, $Y = 1$.

throughout. Up to the region where $\kappa \sim \Lambda$, the function Y represents a summation of the entire Wegner series. When $\bar{u}=1$, there will be no Wegner correction terms generated; the critical theory yields pure power-law behavior. However, as $\kappa \sim \Lambda$, the system may no longer be thought of as critical, and the system crosses over to the classical limit $Y=1$. In the case for which $\bar{u}=0.01$, the system will show power-law behavior over a limited range (dashed line); the effect of including just the first Wegner correction term is also shown (dotted line). Note that there is a region over which the system appears to exhibit pure power-law behavior (i.e., the graph appears linear), well into the range where the first Wegner correction is important. Data analyzed in this region could easily seem to show such power-law behavior but with exponents a few percent above the actual (and expected) asymptotic results. Thus, great care must be taken in interpreting results from measurements taken in the critical region. Such "effective exponents" (e.g., $\beta \approx 0.35$) will be nonuniversal, varying from substance to substance as $\bar{u}$ varies, and, of course, range dependent.

In Fig. 2, we show the coexistence curve for our crossover van der Waals model. The solid curve represents the coexistence curve crossing over from its classical behavior far away from the critical temperature to its Ising-like asymptotic power-law behavior very close to the critical temperature. Note that the location of the true critical point is shifted from the value implied by the classical van der Waals equation, a phenomenon noticed by many investigators when analyzing experimental data [22].

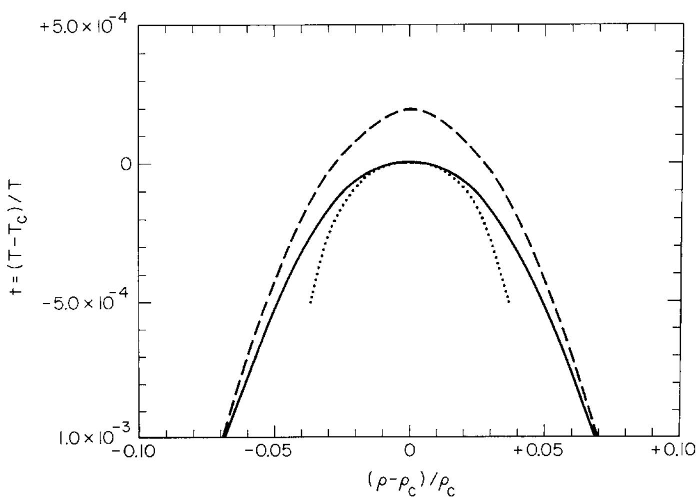

Fig. 2. Plot of the coexistence curve of the crossover van der Waals model. The dashed line denotes expected classical behavior; the dotted line, the asymptotic power law. $\Lambda^2 = \bar{u} = 0.1$.

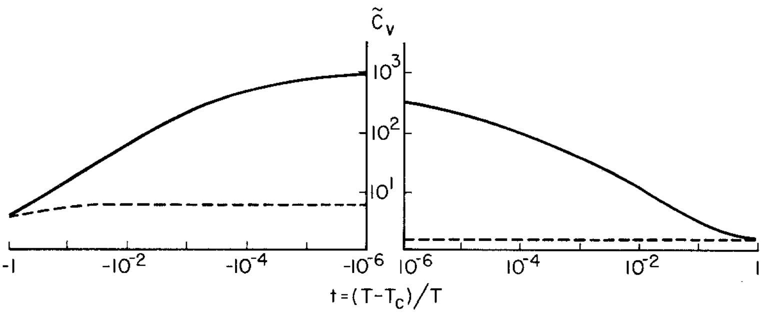

Fig. 3. Log–log plot of the specific heat at constant density for the crossover van der Waals model with ideal-gas background, along the critical isochore above and below the critical temperature. The dashed line shows expected classical behavior. $\Lambda^2 = \bar{u} = 0.1$.

Figure 3 shows the specific heat at constant volume at $\rho = \rho_c$ both above and below the critical temperature; for simplicity, we have assumed an ideal-gas background in C_V. Here, the nonscaling behavior due to the function K is clearly evident; the singular specific heat crosses over to different values in the classical limit above and below T_c as is necessary to obtain agreement with experiment [13].

Figure 4 demonstrates an affect of the asymmetric contributions to the free energy and shows the necessity for defining the scaling field $\Delta\tilde{\mu}$ carefully; we have required that it be zero along the critical isochore in the classical region. In the classical theory there is a jump discontinuity in the

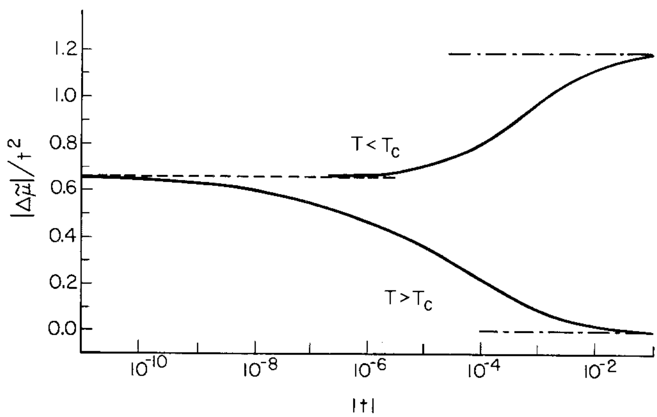

Fig. 4. Semilog plot of $|\Delta\tilde{\mu}|/t^2$ vs t. The upper graph is for the coexistence line; the lower graph, for the critical isochore. The dashed line shows the limiting critical behavior; the broken line, the classical limits. $\Lambda^2 = \bar{u} = 0.1$.

second derivative at the critical point [2]; in the asymptotic critical limit, however, the crossover theory predicts a continuous second derivative as required by naive scaling theory [11].

7. SUMMARY

We have presented here a crossover theory that is derivable from and fully consistent with the renormalization-group theory. By construction, the leading as well as correction-to-scaling terms in the critical region are correctly generated, as are the nonscaling contributions crucial to understanding, for example, the specific heat. The theory introduces the constants $\bar{u}$ and Λ, which determine the size of the asymptotic scaling region and the limit of validity for the Wegner series, respectively. Also by construction, the theory correctly reproduces the classical limit.

Finally, the consistency of the theory with RG calculations frees the theory from the anomalous behavior associated with the switching function approach [23] and from the lack of internal consistency associated with phenomenological crossover models [24, 25]. The theory does not have to be altered, for example, in order to generate the correct Wegner amplitudes and nonscaling behavior.

It remains, of course, to compare the predictions of the theory with experiment. In progress is a comparison with experimental data for carbon dioxide. In addition, it is expected that the theory can be easily extended to fluid mixtures. This work is also in progress.

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