

Expanded Formulation of Thermodynamic Scaling in the Critical Region

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A description of the thermodynamic properties in the critical region of a physical system is obtained from a scaled expression for the free-energy $F(\rho, T)$. In general, a nonsymmetric coexistence curve is predicted, with the symmetric case (e.g., magnets) included as a special example. For fluids, deviations from symmetry give rise to an expression for the average density below the critical point nonlinear in the temperature near T_c (in contrast to the usual "law of rectilinear diameter"); these asymmetries also contribute to the discontinuity in the specific heat along the critical isochore. To lowest order, the formulation reduces to Widom's homogeneous scaling; the classical equations of state of the van der Waals type are incorporated as a special case.

Key words: Critical region; equation of state; liquid-gas transition; phase boundary; phase transition; thermodynamic scaling.

1. Introduction

The Widom-Kadanoff-Domb scaling hypothesis [1–3]¹ provides a qualitative characterization for the thermodynamic features of a second-order phase transition [4]. Scaling incorporates the usual power law forms for the various physical anomalies and more generally serves as a lowest order asymptotic description close to the critical point [5]. Such limiting behavior has been found in various mathematical models and also appears to be valid in real systems.

Despite the relative success of the scaling approach, there remains a definite need for a more global picture of the critical region. This is evident during the analysis of bulk thermodynamic data where there exists first the problem of determining those physical quantities which satisfy the basic conditions required by simple scaling. For some systems, this selection is easily based upon some known/intrinsic physical property (symmetry); whereas for others, the actual choice is less certain [5]. The determination is further complicated by the secondary problem, that of estimating the actual range over which scaling remains valid [6].

These difficulties are particularly evident in the application of the scaling description to real fluids near their critical point [4]. Here there is some experimental indication of a partial anti-symmetry about the critical isochore in the chemical potential μ – number density ρ representation not present with either the pressure p or the specific volume v coordinates. It is also known,

however, that the phase boundary lacks this same symmetry in any set of variables. The coexistence curve is rather asymmetric about the critical isochore with such deviations being described by the empirical "law of rectilinear diameter." Despite the fact that this nonsymmetric behavior cannot be accommodated within the usual lowest order scaling description, the fluid data appear to scale in the preferred μ – ρ coordinates over a rather large region about the critical point (in a density range of ± 30 percent and a temperature width of several percent from their reduced critical values [4]).

An understanding and resolution of such behavior is hampered by an almost complete ignorance of what is beyond the lowest order scaling description. Since any results will be biased by the neglect of unknown terms, one cannot hope to extract any more than a simple qualitative picture from the experimental data without some knowledge as to the structure of corrections to the asymptotic scaling form. The present article represents an attempt to gain some insight into the structure of such terms. The idea was to construct a "model" calculation incorporating modification of the usual scaling formulation. Based upon an extension of classical thermodynamic ideas, the scheme describes systems lacking any known or simple symmetry and extends a scaling interpretation over an enlarged region about the transition. The approach allows for the first time discussion of the various contributions arising from asymmetry and higher ordered corrections to the asymptotic scaling behavior and their influence on observable physical properties. (After completing the

¹ Figures in brackets indicate the literature references at the end of this paper.

work reported here, we learned that Domb and Gaunt have looked at the structure of correction terms to the completely symmetric Ising model equation of state [7].)

It should be pointed out, however, that the formulation given here is just one possible way of going beyond simple asymptotic scaling. For this reason, it is most important to emphasize the underlying formal structure rather than any of the individual numerical results. While the discussion is applied to fluid systems, the approach is easily adopted to other physical situations. The magnetic problem, with a completely symmetric phase boundary, has been discussed elsewhere [8].

2. Formulation

Our approach is based upon two relatively simple observations. Just as in Widom's original hypothesis [1], classical thermodynamics suggests the framework of our analysis. First, recall that from a free-energy function analytic in two physical variables, density ρ and temperature T , one will obtain an equation of state exhibiting in general a nonsymmetric phase boundary, deviations from a completely symmetric coexistence curve giving rise to a finite slope of the rectilinear diameter. With such behavior, however, one also acquires the classical (van der Waals-like) and quite incorrect description of the critical region [9]. Thus, instead of using such physical variables, we shall follow Widom [1] and assume the thermodynamic properties near the critical point are appropriately described in terms of one intensive physical quantity and one suitably reduced variable x . Moreover, the description is to be consistent with the homogeneity hypothesis, i.e., all functions are to be regular and of a general homogeneous form [5]. The existence of such nonclassical forms has been demonstrated in various model calculations where the scaling behavior appears as the first term in an expansion about the critical point. As an example, Cooper and Green [10] found that the appropriate free-energy of the Bose fluid is a function of the reduced temperature $t = (T - T_c)/T_c$ and a reduced variable $x = t |\Delta\rho|^{-1/\beta}$, $\Delta\rho = (\rho - \rho_c)/\rho_c$ with the scaling form as the dominant term in an expansion containing higher ordered homogeneous terms. (Gaunt and Domb [7] have suggested a similar structure which applies to the Ising model.) As our second point, we shall assert that in general the free-energy density in the critical region is given by a convergent expansion of the form

$$F(\rho, T) - F_0(\rho, T) = |\Delta\rho|^{\delta+1} \sum_{s=1}^{\infty} (\Delta\rho)^{s-1} f_s(x) \quad (1)$$

where $x = t |\Delta\rho|^{-1/\beta}$. Here both $1/\beta$ and δ are to be arbitrary constants (not necessarily integer) and $F_0(\rho, T)$ denotes any smooth analytic part of the free-energy near the transition ρ_c, T_c . It is implicitly assumed that the function $F(\rho, T)$ is single valued everywhere and satisfies the well-known convexity conditions for thermodynamic stability [5]. The set of functions

$\{f_s(x)\}$ are to be "well behaved" in the variable $x = t |\Delta\rho|^{-1/\beta}$ over the real interval of interest ($\min x_0^{\pm} \leq x \leq +\infty$). (We require only that $F(\rho, T)$ satisfy the physical conditions of continuity and differentiability in the single-phase region with each $f_s(x)$ analytic for x less than some finite constant R (see below).) Equivalently, one could take similar expressions for the chemical potential $\mu(\rho, T)$ and the pressure $p(\rho, T)$ about the critical point $\rho = \rho_c, t = 0$:

$$\mu(\rho, T) = \mu_c + \mu_0(t) + |\Delta\rho|^{\delta-1} \sum_{s=1}^{\infty} (\Delta\rho)^s \mu_s(x), \quad (2)$$

$$p(\rho, T) = p_c + p_0(t) + |\Delta\rho|^{\delta-1} \sum_{s=1}^{\infty} (\Delta\rho)^s p_s(x). \quad (3)$$

Both thermodynamic forces are to be well-behaved everywhere in the single-phase region and also on the phase boundary (except perhaps at the critical point). These expressions are also consistent with the experimental observation that both p and μ have continuous first derivatives across the critical isochore. The dominant $s=1$ term of these expansions represent the usual asymptotic scaling expressions. The functions $\mu_s(x)$ and $p_s(x)$ are not independent but are themselves related to the set $\{f_s(x)\}$ through the thermodynamic relations

$$p(\rho, T) = \rho^2 \left. \frac{\partial F(\rho, T)}{\partial \rho} \right|_T \quad (4)$$

and

$$\mu(\rho, T) = \left(1 + \rho \frac{\partial}{\partial \rho} \right)_T F(\rho, T). \quad (5)$$

The form of $F_0(\rho, T)$ must be consistent with the expressions for μ and p . The first few important relations of this hierarchy are that

$$\left[\delta + 1 - \frac{x}{\beta} \frac{\partial}{\partial x} \right] f_1(x) = \mu_1(x) = \rho_c^{-1} p_1(x) \quad (6)$$

and

$$\rho_c^{-1} p_2(x) - \mu_2(x) = \left[\delta - \frac{x}{\beta} \frac{\partial}{\partial x} \right] f_1(x). \quad (7)$$

2.1. Two-Phase Region

Below the critical temperature, $t < 0$, we seek simultaneous (non-trivial) solutions to the conditions for thermodynamic stability of coexisting phases, ρ_L and ρ_G ,

$$p(\rho_L, T) = p(\rho_G, T) \text{ and } \mu(\rho_L, T) = \mu(\rho_G, T). \quad (8)$$

Denoting the two branches by $\rho_L - \rho_c = \Delta\rho^+$ and $\rho_G - \rho_c = \Delta\rho^-$, with $\Delta\rho^{\pm} = \pm (|t|/|x^{\pm}|)^{\beta}$, the shape of the phase boundary is found by expanding eqs (2) and (3) in a Taylor series about x_0^{\pm} respectively, algebraic consistency requiring that

$$x^{\pm} = x_0^{\pm} + x_1^{\pm} |t|^{\beta} + x_2^{\pm} |t|^{2\beta} + \dots \quad (9)$$

Matching the various powers in $|t|^\beta$ we find that

- (i) $x_0^+ = x_0^- = -x_0$, with both $\mu_1(x)$ and $p_1(x)$ vanishing at $x = -x_0$;
- (ii) $x_1^+ = -x_1^- = x_1$ where $x_1 = |-x_0|^{1-\beta}$

$$\left[\frac{p_3(x) - \rho_c \mu_3(x)}{\left(\beta(\delta+1) - x \frac{\partial}{\partial x} \right) (p_2(x) - \rho_c \mu_2(x))} \right]_{x=-x_0};$$

- (iii) in general $x_r^+ = (-1)^r x_r^- = x_r$.

Thus we identify $\mu_1(x)$ with Griffith's [5] $h(x)$ function and the condition that $h(x = -x_0)$ vanish along the phase boundary.

With the boundary condition $\mu_1(-x_0) = 0$ we can also solve the differential equation (6) for $f_1(x)$. The homogeneous solution is a constant times $|x|^{\beta(\delta+1)}$; the general solution may be written as

$$f_1(x) = x^{\beta(\delta+1)} \left[\frac{f_1(-x_0)}{|-x_0|^{\beta(\delta+1)}} - \beta \int_{-x_0}^x dy \frac{\mu_1(y)}{y^{\beta(\delta+1)}} \right]. \quad (10)$$

The difference between the two coexisting densities is found to be given by

$$\rho_L - \rho_G = \left[\frac{2}{|-x_0|^\beta} \right] |t|^\beta + \left[\frac{\beta(\beta+1)}{2} \left(\frac{x_1}{x_0} \right)^2 + \frac{x_2}{x_0} \right] |t|^{3\beta} + \dots \quad (11)$$

Deviations from a completely symmetric coexistence curve are described by the mean density of the two phases

$$\bar{\rho} = \frac{1}{2} (\rho_L + \rho_G) = \rho_c + \left[\frac{-\beta x_1}{|-x_0|^{\beta+1}} \right] |t|^{2\beta} + O(|t|^{4\beta}). \quad (12)$$

This is equivalent to the usual "law of rectilinear diameter" in the classical case ($\beta = 1/2$), but has the curious feature that for real fluids ($\beta < 1/2$) the average density ρ is curved and comes into the critical point with zero slope. See figure 1. When $x_1 = 0$, the phase boundary is symmetric to this order.

It is also possible to describe the form of the vapor pressure curve using the equation for $p(\rho, T)$

$$p_{\text{coex.}}(\rho, T) = p_c + p^*(t) + |t|^{\beta(\delta+1)} \left[\frac{p_2(-x_0)}{|-x_0|^{\beta(\delta+1)}} + O(t^{2\beta}) \right] \quad (13)$$

with a similar expression for the chemical potential in the two-phase region (replace p_s by μ_s). Here $p^*(t)$ is a smooth analytic function in the temperature.

While the specific heat C_v in the two-phase region can be obtained from the free-energy $F(\rho, T)$, it is

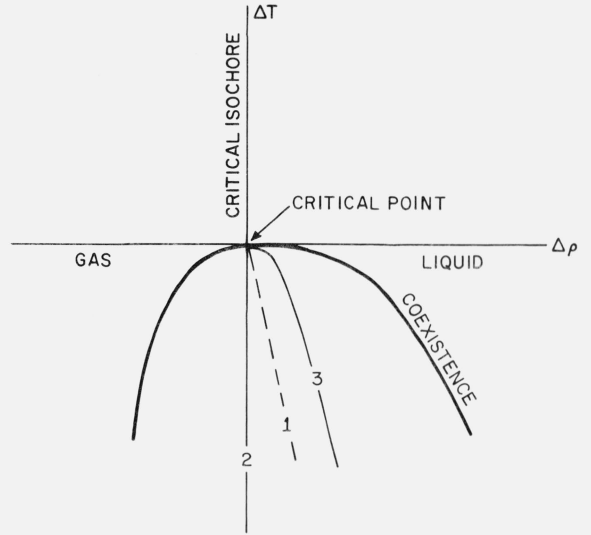


FIGURE 1. Locus of mean densities for coexisting Phases.

- Curve 1 (dashed line)—usual rectilinear diameter;
- Curve 2 (vertical line)—line of mean density of completely symmetric phase boundary like that supposed by lowest order scaling;
- Curve 3 (solid line)—locus of mean densities suggested by eq (12).

perhaps more interesting to look at the individual contributions from the chemical potential μ and pressure p as exhibited in the thermodynamic identity (Yang and Yang [11])

$$\rho C_v = T \left(\frac{\partial^2 p}{\partial T^2} \right)_\rho - \rho T \left(\frac{\partial^2 \mu}{\partial T^2} \right)_\rho. \quad (14)$$

As the critical point is approached from below T_c along the critical isochore $\rho = \rho_c$, the anomalous temperature variation is given by

$$\frac{\rho_c C_v}{T} = A_- \cdot |t|^{\beta(\delta+1)-2} + O(t^{\beta(\delta+3)-2}) \quad (15)$$

where

$$A_- = \beta(\delta+1) \{ \beta(\delta+1) - 1 \} \left[\frac{p_2(-x_0) - \rho_c \mu_2(-x_0)}{|-x_0|^{\beta(\delta+1)}} \right].$$

Here the expressions for the pressure (13) and chemical potential on the phase boundary have been used and it has been assumed that the difference $p_2(x) - \rho_c \mu_2(x)$ does not vanish at $x = -x_0$. The asymptotic behavior of the specific heat is thus characterized by a critical exponent $\alpha = 2 - \beta(\delta+1)$ and a coefficient determined entirely by the form of $f_1(x)$ at $x = -x_0$ (see eq (7)). In the simple scaling formulation where $\mu(\rho, T)$ is regular, the divergence of the specific heat along the critical isochore ($T < T_c$) comes entirely from the $(\partial^2 p / \partial T^2)_{\rho_c}$ contribution. This formulation permits contributions from either the pressure and chemical potential by treating both thermodynamic forces on an equal basis.

2.2. Single-Phase Region

All of the thermodynamic properties of the homogeneous fluid in the one-phase region can be obtained directly from the free-energy $F(\rho, T)$. We assume that no higher order discontinuities exist anywhere in this region including the critical isochore $x=\infty$. This implies that the expression for $\mu(\rho, T)$ and $p(\rho, T)$ in the (x, t) plane exist and are everywhere convergent for large $R < x \leq \infty$.

In general, the isothermal compressibility K_T is given by

$$[\rho^2 K_T]^{-1} = \left(\frac{\partial \mu}{\partial \rho T} \right) \\ = \frac{|\Delta \rho|^{\delta-1}}{\rho_c} \sum_{s=1}^{\infty} (\Delta \rho)^{s-1} \left[(\delta + s - 1) - \frac{x}{\beta} \frac{\partial}{\partial x} \right] \mu_s(x) \quad (16)$$

with the thermodynamic stability [5] requiring that K_T be everywhere non-negative. The dominant thermodynamic behavior near the critical isochore (x large) is given by the leading term in this expression ($s=1$) and is like that found from simple scaling. As the critical point is approached along the coexistence curve within the single-phase region, the compressibility diverges as $|t|^{-\gamma'}$ where $\gamma' = \beta(\delta-1)$, provided $\mu_1'(-x_0) \neq 0$.

The thermodynamic behavior of the specific heat in the homogeneous phase is given by

$$C_v = -T(\partial^2 F / \partial T^2) \rho,$$

which may be written as

$$C_v = \frac{1+t}{\rho_c T_c} \sum_{s=1}^{\infty} |t|^{\beta(\delta+s-1)-2} \left[\frac{\rho_s''(x) - \rho_c \{ \mu_s''(x) + \mu_{s-1}''(x) \}}{x^{\beta(\delta+s-1)-2}} \right] \quad (17)$$

with $\mu_0(x)=0$ (neglecting the smooth contribution from $F_0(\rho, T)$). Since $p_1(x) = \rho_c \mu_1(x)$, the lowest possible contribution to the specific heat must come from an $s \geq 2$ term in this expression. Here in the single phase, just as in the two-phase region, the available experimental evidence suggests that the pressure term $(\partial^2 p / \partial T^2) \rho_c$ is much larger than the chemical potential term [12]. About the critical isochore above T_c , the specific heat varies as $|t|^{-\alpha}$, where $\alpha = 2 - \beta(\delta + s - 1)$, with s determined by the first nonvanishing term in the limit as $x \rightarrow \infty$. (The anomaly in the specific heat along the critical isochore is also given by $F_r |t|^{-\alpha}$, where $\alpha = 2 - \beta(\delta + r)$ and F_r denotes the limit of $f_r(x) \cdot x^{-\beta(\delta+r-1)}$ as $x \rightarrow \infty$.) Such structure admits the possibility of different values for the critical indices α and α' . If, for example, the leading $s'=2$ were finite in the two-phase region and then vanish above T_c at large x [see eqs 15, 17], s

would be greater than 2 and thus the difference $|\alpha - \alpha'| = \beta|s - s'|$ could be greater than zero.

3. Discussion

The extended formulation of thermodynamic scaling presented here provides a quite general description for the critical region of a fluid. The formalism proceeds beyond the usual lowest order asymptotic behavior and accommodates both the chemical potential and pressure as equivalent physical variables. Within the description it is possible to note contributions from the various higher ordered terms ($s > 1$) and of the two quantities ρ, μ to the various physical anomalies. We found, for example, that the difference between the potential and pressure variables is not only reflected in the shape of the coexistence curve (as determined by the value of x_1), but also enters into the leading behavior of the specific heat.

We also expect extended scaling to be valid beyond the asymptotically small range of simple scaling, with contributions from the additional terms affecting the determination of the values of the critical indices away from the actual critical point. For example, the experimentally determined shape of the coexistence curve β^* would be greater or less than the true β , the modification depending upon both the sign and magnitude of the additional terms of eq (1).

In the rather special cases where $1/\beta$ is an even integer, the formulation recovers the classical thermodynamic description of a van der Waals system. For $\beta = 1/2$, this is just the familiar parabolic coexistence curve of the mean-field result, with the usual rectangular diameter $\bar{\rho} = \rho_c + \rho_2 |t|$.

As mentioned before, any comparison of these results to the physical features must remain somewhat qualitative. This is because the formulation is essentially analytic everywhere and must therefore suffer the same defects as all "classical" equations of state. However, we believe the utility of this analysis lies in the display of certain features which must eventually be contained in any complete thermodynamic description of the critical region.

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