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Extended Thermodynamic Scaling from a Generalized Parametric Form

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A generalization of the parametric representation for thermodynamic scaling is proposed, introducing a new critical exponent ϵ. Expansions about the critical point are deduced for the fluids, and to lowest order the asymptotic power-law forms are recovered. An exponent $1-\alpha'$ is obtained for the diameter of the coexistence curve. Experimental data are shown to support the predicted forms.

The Widom[1]-Kadanoff[2]-Domb[3] scaling hypothesis provides a successful characterization of thermodynamic behavior about the critical point. The resulting scaled equation of state,[4] which incorporates the power laws for the various thermodynamic anomalies, has been used to describe the critical region of a wide range of substances.[5] This description is however valid only in a neighborhood close to the actual critical point and must therefore be regarded as a first approximation in an expansion about that point. The structure of the expansion is known only for the classical models and Bose gas[6]; and recently, Domb has suggested a scaled expansion for the Ising models.[7] In this Letter, we are concerned with the expansion for real physical systems, especially that for the fluids.

We propose here expansions for the thermodynamic properties in the critical region which extend beyond the range of ordinary scaling. These expansions are developed from a generalization of the Josephson[8]-Schofield[9] parametric reformulation of thermodynamic scaling. A new critical exponent ϵ is introduced and related to the existing ones by making use of an invariance principle suggested by Griffiths and Wheeler.[10] In comparing this expanded description with experiment, we identify the leading term in each expression with that given by simple scaling; we find that the asymmetry typical of fluids enters only in higher order. Predictions for the terms past the leading ones are consistent with the available experimental information.

Choice of variables.—Scaling of the chemical potential difference $\mu(\rho,T)-\mu(\rho_c,T)$, as suggested by Widom[1] and applied by some of us[11] to fluid systems, has a disadvantage in that nothing *a priori* is known about the analytic nature of $\mu(\rho_c,T)$. Only in certain lattice models is it known to be free of anomalies. Here we assume no more than the existence of the first derivative $(\partial\mu/\partial T)_\rho$ at the critical point. Contrary to previous usage,[5,11] the physical variables are measured relative to their critical-point value; thus, the symbol $\Delta\mu$ is to be interpreted as $\Delta\mu=\mu(\rho,T)-\mu(\rho_c,T_c)$.

Griffiths and Wheeler (GW)[10] have shown that it is advantageous to discuss critical phenomena in terms of intensive "field" variables rather than extensive quantities since such a field has equal values in the coexisting phases. For independent variables we choose the chemical potential $\Delta\mu$ and the temperature ΔT – basically because this choice leads to a large range for ordinary scaling.[11] For a dependent variable we choose the potential $P^*(\Delta\mu, \Delta T)$ such that $dP^* = \Delta\rho d(\Delta\mu) + \Delta s d(\Delta T)$, where s and ρ are the entropy and number densities, respectively. Physically this potential P^* is the difference between the pressure on the thermodynamic surface and the pressure on a plane tangent to this surface at the critical point $\Delta P = \rho_c \Delta\mu + s_c \Delta T$.

GW[10] have pointed out that in this space of intensive variables there is but one direction of unique physical significance, namely that of the vapor-pressure curve or critical isochore at the critical point. This direction is characterized by $\Delta\mu = c_2 \Delta T$, where $\rho_c c_2 = c_1 - s_c$; c_1 is the critical-point limit value of the quantity $(S_g - S_l)/(V_g - V_l)$ occurring in the Clapeyron equation. The quantity $\mu^* = \Delta\mu - c_2 \Delta T$ measures the distance *away* from this preferred direction and is closely related to Widom's[1] "$\Delta\mu$" $= \mu(\rho, T) - \mu(\rho_c, T)$. As a measure of the distance *along* this preferred direction, one can select any other linear combination of $\Delta\mu$ and ΔT. The transformation from the variables Δp, $\Delta\mu$, ΔT to the set P^*, μ^*, T^* can be written as

$$\begin{aligned} \Delta p &= P^* + \rho_c \mu^* + c_1 T^*, \\ \Delta\mu &= \mu^* + c_2 T^*, \\ \Delta T &= c_3 \mu^* + T^*. \end{aligned} \tag{1}$$

Here the diagonal elements of the transformation matrix have been normalized to unity. The value of c_3 is unspecified.

Generalized parametric representation. – Schofield[9] has phrased scaling in terms of parametric variables, r and θ, where r is the distance from the critical point and θ a measure along a contour of fixed r. For our variables P^*, μ^*, T^*, his parametric equations are of the form

$$P^* = r^{\beta(\delta+1)} p(\theta), \quad \mu^* = r^{\beta\delta} h(\theta), \quad T^* = r t(\theta). \tag{2}$$

The only physical singularities occur at the actual critical point, $r=0$, with the power laws incorporated into the algebraic structure. The expressions proposed by Schofield for the functions $p(\theta)$, $h(\theta)$, $t(\theta)$ all satisfy the more general symmetry conditions stated by Josephson[8] for the magnetic case.

Our proposed generalization of these ideas follows from noting that it is possible to replace r by r^ϵ without affecting the physical consequences; secondly, that since all physical behavior away from the critical point or origin is regular, the functions p, h, t may also exhibit smooth, analytic dependence upon the r variable; and finally, that the special symmetry requirements in the θ dependence of the functions may be relaxed.[12] Thus, we propose

$$\begin{aligned} P^* &= r^{\beta(\delta+1)\epsilon} p(r, \theta), \\ \mu^* &= r^{\beta\delta\epsilon} h(r, \theta), \\ T^* &= r^\epsilon t(r, \theta). \end{aligned} \tag{3}$$

It follows that $\Delta\rho = r^{\beta\epsilon} m(r, \theta)$. The functions p, h, t, and m are assumed to be analytic in r everywhere, including the origin (no confluent singularities).

The physical consequences of this expanded formulation are obtained by eliminating the parametric variables on the various contours of interest. For convenience, we set the constant c_3 equal to zero [see Eq. (1)]. Thus, along the critical isotherm, the solutions of $\Delta T = 0$, when substituted into the equations for $\Delta\mu$ and $\Delta\rho$, yield

$$\Delta\mu = \Delta\rho |\Delta\rho|^{\delta-1} \{D_1^\pm + D_2^\pm |\Delta\rho|^{1/\beta\epsilon} + D_3^\pm |\Delta\rho|^{2/\beta\epsilon} + \cdots\}. \tag{4a}$$

Similarly, from the equality of P, μ, and T in the two phases, the phase boundary can be constructed:

$$\Delta\rho = |\Delta T|^\beta \{B_1^\pm + B_2^\pm |\Delta T|^{1/\epsilon} + B_3^\pm |\Delta T|^{2/\epsilon} + \cdots\}. \tag{4b}$$

Here [in (4a) and 4(b)] the ± refers to the two physical branches above/below the critical density. On the critical isochore, $\rho = \rho_c$, and along the vapor pressure curve we find

$$\Delta\mu = c_2 \Delta T + |\Delta T|^{\beta\delta} \{H_1^\pm + H_2^\pm |\Delta T|^{1/\epsilon} + H_3^\pm |\Delta T|^{2/\epsilon} + \cdots\}, \tag{4c}$$

$$\Delta p = s_c \Delta T + \rho_c \Delta\mu + |\Delta T|^{2-\alpha} \{P_1^\pm + P_2^\pm |\Delta T|^{1/\epsilon} + \cdots\}, \tag{4d}$$

$$\rho c_v / T = |\Delta T|^{-\alpha} \{A_1^\pm + A_2^\pm |\Delta T|^{1/\epsilon} + A_3^\pm |\Delta T|^{2/\epsilon} + \cdots\}, \tag{4e}$$

where the ± refers to temperatures above/below T_c.

In contrast to the equations of simple scaling,[1,4] these expressions (4) do not contain unspecified regular background terms. Only the term linear in ΔT must have the same coefficient above and below T_c. These expansions contain the additional exponent ϵ; its choice affects the physical result beyond the lowest order.

Value of ϵ.—In the transformation of P^*, μ^*, T^*, the direction of the third basis vector was fixed along that of the vapor-pressure curve and critical isochore at the critical point. Since there is no other physically preferred direction,[10] any linear combination of μ^* and T^* should have the same structure as T^* itself. Thus, $r^{\beta\delta\epsilon}h(r,\theta)+r^{\epsilon}t(r,\theta)$ should be of the form $r^{\epsilon}t'(r,\theta)$ with t' again analytic. This requires that $\beta\delta\epsilon-\epsilon$ be an integer, for which we propose the simplest choice,

$$(\beta\delta-1)\epsilon=1, \tag{5}$$

and thus, $\beta+1/\epsilon=1-\alpha'$.

Symmetry.—For the lattice systems there are basic symmetry conditions which the various functions must fulfill[8]: $m(r,\theta)$ and $h(r,\theta)$ must be antisymmetric in θ, while $p(r,\theta)$ and $t(r,\theta)$ must be symmetric. Thus, in the expressions (4), $B_i^+=B_i^-$, $D_i^+=D_i^-$ while $H_i^{\pm}=0$ for all i.

Without any such symmetry requirements, one finds that all of the coefficients, including those of the leading terms, may be different about the transition. Moreover, along the critical isochore, the leading term in $\partial^2 p/\partial T^2$ will behave as the leading term in $\partial^2\mu/\partial T^2$, both varying as $|\Delta T|^{\beta\delta-2}$. This is rather different from the predictions of simple scaling where $\partial^2\mu/\partial T^2$ is regular, while $\partial^2 p/\partial T^2$ goes as $|\Delta T|^{-\alpha}$. However, experimental μ-ρ curves appear to be antisymmetric to lowest order, and thus D_1^+ must equal D_1^-. This equality follows from our Eq. (4) if, to lowest order in r, the functions $h(r,\theta)$ and $m(r,\theta)$ are antisymmetric in θ, while $t(r,\theta)$ and $p(r,\theta)$ are symmetric. These conditions in turn imply that the coexistence curve has a symmetric tip, $B_1^+=B_1^-$—a fact consistent with experiment. A less obvious but important consequence of this symmetry condition is that the coefficient $H_1^{\pm}$ of the leading term in the expansion of $\Delta\mu$ along the critical isochore will vanish. Hence, the leading terms in $\partial^2 p/\partial T^2$ and the specific heat on the critical isochore both diverge with the same exponent α.

This lowest order θ symmetry observed in fluids is an invariant property, i.e., it obtains whatever the value of c_3. Although the most appropriate choice for the Ising models appears to be c_3 identically zero, any other value of c_3 preserves the θ symmetry of the various functions to lowest order in r.

Tests.—Using available experimental data, we have checked the expansions (4) with our choice (5) of ϵ, testing both the lowest-order symmetries and the form of the first correction terms. Evidence for the antisymmetry of the critical isotherm and for the symmetry of the top of the coexistence curve has been given previously.[11,13] Recently obtained pressure data for CO_2 (precise to 2×10^{-5} in reduced pressure) were fitted by various suggested forms for the vapor-pressure curve and critical isochore (see Table I). The simple scaling forms incorporating an analytic background term $A_0(T)$,[11] quadratic in T,[14] are seen to fit the two separate branches quite well. However, such a form does not fit the two combined branches. Allowing the coefficient of the quadratic term to differ above and below T_c improves the fit, but violates the spirit of simple scaling. Without symmetry, extended scaling gives $|\Delta T|^{\beta\delta}$ rather than $|\Delta T|^{2-\alpha}$. However, the

Table I. Critical isochore of CO_2.

Expression used for ΔP ($\beta=0.35$, $\delta=4.5$, $\alpha=0.075$)	$10^5\times$ (Standard deviation of reduced pressure)		
	Vapor pressure $0.88<T/T_c<1$	Crit. isochore $1<T/T_c<1.05$	Two branches combined $0.88<T/T_c<1.05$
$A_{01}\Delta T+A_{02}\Delta T^2+P_1^{\pm}\lvert\Delta T\rvert^{2-\alpha}$ Simple scaling, Refs. 2, 11	3.8	1.9	11.7
$A_{01}\Delta T+A_{02}^{\pm}\Delta T^2+P_1^{\pm}\lvert\Delta T\rvert^{2-\alpha}$ Simple scaling—different coefficients	3.8	1.9	3.2
$c_1\Delta T+P_1^{\pm}\lvert\Delta T\rvert^{2-\alpha}+\rho_c H_2^{\pm}\lvert\Delta T\rvert^{2\beta\delta-1}$ Extended scaling, lowest-order symmetry	2.2	2.0	3.6
$c_1\Delta T+\rho_c H_1^{\pm}\lvert\Delta T\rvert^{\beta\delta}+P_1^{\pm}\lvert\Delta T\rvert^{2-\alpha}$ Extended scaling, no symmetry	14.1	1.8	15.3

fit of such a form to both the separate and combined branches is quite poor. This is consistent with our previously assumed symmetry $H_1^{\pm}=0$, so that the coefficient of this $|\Delta T|^{\beta\delta}$ term vanishes. The resulting expression has $|\Delta T|^{2-\alpha}$ as the leading nonanalytic term and is consistent with the data (see table).

The most direct test of the higher order ϵ-dependent terms comes from the diameter of the coexistence curve. Since the leading term in (4b) vanishes from the sum $\rho_l+\rho_g$, the equation of the diameter is $\bar{\rho}=\frac{1}{2}(B_1^{+}+B_1^{-})|\Delta T|^{1-\alpha'}$ with our choice (5) for ϵ. At the present time, this $|\Delta T|^{1-\alpha'}$ form, where $1-\alpha'\simeq 0.9$, is not distinguishable from the empirical law of rectilinear diameter $\bar{\rho}\sim|\Delta T|$ which has recently been reconfirmed for optically determined coexistence curves of CO_2, N_2O, and $CClF_3$ in the range $0.95 \leq T/T_c \leq 1$.[13] A behavior of the form $1-\alpha'$ has been found by Rowlinson and Widom in a certain asymmetric lattice gas.[15]

A less direct test of the higher terms is made by looking at the critical isotherm. Wallace and Meyer[16] recently reported an exponent $\delta+(2 \pm 0.5)$ for the density dependence of $\mu_l-\mu_g$ on the critical isotherm of He^3. *PVT* data on He^4 also analyzed by them gave roughly the same result. We have constructed a near-critical P-ρ isotherm at 31.013° from Michels' CO_2 *PVT* data.[17] Because this isotherm is not finely enough spaced at $\rho>\rho_c$ to permit direct calculation of μ, the μ-ρ relation (4b) was transformed into one for P-ρ which was then fitted to the data. In a range up to $|\Delta\rho|=0.6$ a good fit was obtained by using an antisymmetric leading term, with an exponent $\delta+1.6$ to $\delta+2.4$ for the correction term. The coefficients D_1^{+} and D_1^{-} are clearly different.

We have also compared our expressions to those suggested by Domb[7] for the two- and three-dimensional Ising models. We could generate a double power series reminiscent of Domb's form by allowing transformation of the potential as well as of the independent intensive variables. There remain, nevertheless, other differences between the two descriptions requiring further study.

Summary.—The extension of thermodynamic scaling proposed here is based upon a generalization of the parametric description for the equation-of-state surface. Certain known experimental facts, as well as the invariance property stated by Griffiths and Wheeler for the independent intensive variables, were used as a guide to its structure:

(1) Scaling appears valid over a wide range in the chemical-potential–temperature–density representation, suggesting μ and T as the preferred independent intensive variables.

(2) The antisymmetry of the critical isotherm and symmetry of the coexistence curve suggest that deviations from symmetric behavior in the other thermodynamic properties must be sought in higher order corrections to simple scaling.

(3) In the intensive thermodynamic space there is a unique physically significant direction, the common direction of the coexistence curve and critical isochore. This may be interpreted as an invariance principle and used to fix the value of a new critical index ϵ.

The formulation presented here displays certain differences from simple thermodynamic scaling, extending the description over an enlarged region of the thermodynamic phase plane about the critical point, and appears to be consistent with the available experimental data.

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