mathematical analysis. The most accurate representation is provided by the two power series (1) and (2). These appear to be the best equations to check theoretical calculations when they become available and to compare various magnetic systems, pure fluids, and critical mixtures.

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PARAMETRIC REPRESENTATION OF THE EQUATION OF STATE NEAR A CRITICAL POINT*

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A parametric representation of the usual thermodynamic variables in the neighborhood of a critical point is proposed in terms of new variables r and θ. The representation is chosen so that the "scaling-law" behavior is entirely contained in the r dependence, the θ dependence being free of critical singularities. Preliminary calculations show that the θ dependence may be chosen to have a rather simple form both in a ferromagnet and in fluids.

It is now widely accepted (though not theoretically established) that Widom's hypothesis,[1] that the free energy of a ferromagnet or a fluid in the neighborhood of its critical point can be expressed as a homogeneous function of two of the thermodynamic variables, is essentially correct. In this Letter we propose a parametric representation of the thermodynamic behavior which automatically satisfies the so-called "scaling-law"[2] relations, which follow from the hypothesis of homogeneity.

Let T be the temperature measured from T_c as zero, let H be the magnetic field in the magnetic case and represent the chemical potential difference $(\mu-\mu_c)$ in the fluid, and let M be the magnetization (magnet) and density deviation $(n-n_c)$ (fluid). We consider the thermodynamic potential $\pi(H,T)$ defined by

$$\pi(H,T)=HM(H,T)-F(M,T)+F(0,0)-S_cT \text{ (magnet)} \quad (1)$$

$$=P(H,T)-P_c-n_cH-S_cT \text{ (fluid)}, \quad (2)$$

where F is the free energy, P the pressure, and S the entropy. Then M is given by $(\partial\pi/\partial H)_T$ and $(S-S_c)$ by $(\partial\pi/\partial T)_H$.

The transformation we suggest arises from the knowledge[3] that $\pi(H,T)$ is a well behaved function of H for a given T and the plausible assumption that it is also a well behaved function of T away from the coexistence curve, $H=0$, $T<0$. Thus we expect $\pi(H,T)$ to be well behaved along any contour leading from one side of the coexistence curve to the other. This suggests that if we transform to variables r, which gives a measure of the distance of a point (H,T) from the critical point, and θ, which measures the distance along a contour of constant r, then the singular behavior at the critical point should be determined by the behavior as $r\to 0$ and that the thermodynamic functions should be well behaved in θ.

The transformation proposed is

$$H=ar^{\beta\delta}\theta(1-\theta^2), \quad (3)$$

$$T=r(1-b^2\theta^2), \quad (4)$$

where a and b are disposable parameters with a

>0, $b>1$. Thus $\theta=0$ represents the critical isochore (strictly $\mu=\mu_c$ in the fluid case), $\theta=\pm1$ the two sides of the coexistence curve, and $\theta=\pm b^{-1}$ the two parts of the critical isotherm for $H \gtrless 0$.

If, now, we assume that π as a function of r and θ has the form

$$\pi(r,\theta)=r^{\beta(\delta+1)}p(\theta) \tag{5}$$

then we obtain by a transformation of variables

$$M=\partial\pi/\partial H=r^{\beta}m(\theta), \tag{6}$$

$$S-S_c=\partial\pi/\partial T=r^{\beta(\delta+1)-1}s(\theta), \tag{7}$$

where

$$m(\theta)=[2\beta(\delta+1)b^2\theta p(\theta)+(1-b^2\theta^2)p'(\theta)]/aD(\theta), \tag{8}$$

$$s(\theta)=[\beta(\delta+1)(1-3\theta^2)p(\theta)-\beta\delta\theta(1-\theta^2)p'(\theta)]/D(\theta), \tag{9}$$

$$D(\theta)=1+(2b^2\beta\delta-3-b^2)\theta^2-b^2(2\beta\delta-3)\theta^4. \tag{10}$$

Furthermore, the susceptibility (compressibility) and the specific heat may be written in terms of $m(\theta)$ and $s(\theta)$, respectively, as

$$(\partial M/\partial H)_T=a^{-1}r^{-\beta(\delta-1)}[2\beta b^2\theta m(\theta)+(1-b^2\theta^2)m'(\theta)]/D(\theta), \tag{11}$$

$$(\partial S/\partial T)_H=r^{\beta(\delta+1)-2}\{[\beta(\delta+1)-1](1-3\theta^2)s(\theta)-\beta\delta\theta(1-\theta^2)s'(\theta)\}/D(\theta). \tag{12}$$

Thus it will be seen that writing $\pi(r,\theta)$ in the form of Eq. (5) leads to "scaling-law" behavior: Along the critical isochore $r=T$, so that $(\partial M/\partial H)_T \propto T^{-\gamma}$ with $\gamma=\beta(\delta-1)$ and $(\partial S/\partial T)_H \propto T^{-\alpha}$ with $\alpha=2-\beta(\delta+1)$, while on the critical isotherm

$$r=\{b^3H/a(b^2-1)\}^{1/\beta\delta}$$

so that $H\propto M^{\delta}$, and on the coexistence curve $r=(b^2-1)^{-1}|T|$, $M\propto|T|^{\beta}$.

The functions $p(\theta)$ and $m(\theta)$ have the following properties. Since $\pi(H,T)$ is single valued[3] on the coexistence curve, $p(1)=p(-1)$. For a magnet $p(\theta)$ is an even function of θ. We call attention to the fact that scaling in itself does not require that $p(\theta)$ be an even function for a fluid; however, experiments[4] indicate at least that the critical isochore $n=n_c$ follows $\mu=\mu_c$ so that $p'(0)=0$. Thus we can write generally $m(\theta)=\theta g(\theta)$ with $g(0)$ finite.

The critical behavior in the (r,θ) space introduced above is summarized in Table I where the constants of proportionality are related to the parameters of this representation.

One virtue of the transformation, Eqs. (3) and (4), is that it takes a particularly simple form for mean field theory for which the equation of state in the critical region is

$$C_0H=MT+B^{-2}M^3. \tag{13}$$

With $\beta=\frac{1}{2}$, $\delta=3$, this is clearly satisfied by $g(\theta)$ equal to a constant g with a and b satisfying $g=aC_0$, $(b^2-1)=a^2C_0{}^2B^{-2}$.

In general, once $m(\theta)$ is known, the free energy function $p(\theta)$ may be obtained by quadrature:

$$\frac{d}{d\theta}(1-b^2\theta^2)^{-\beta(\delta+1)}p(\theta)=a(1-b^2\theta^2)^{-\beta(\delta+1)-1}m(\theta)D(\theta). \tag{14}$$

[An exceptional case is $\beta(\delta+1)=2$, $\alpha=0$. Here one may use an argument similar to that of Widom[1] to show that $\pi(r,\theta)$ contains an additional term proportional to $(1-2\beta)r^2(1-b^2\theta^2)^2\ln r$, in which case the specific heat has a logarithmic singularity unless $\beta=\frac{1}{2}$. This will be treated in detail in a forthcoming paper. It does not affect any arguments relating to derivatives at constant T.]

The transformation (3), (4) has been applied to (a) the data of Ho and Litster[5] on the insulating ferromagnet chromium tribromide, and (b) the data collected by Green, Vicentini-Missoni, and Levelt Sengers[4] for a number of fluids. In the latter case the results must be regarded as preliminary since the values we used were obtained by drawing smooth curves through their published scaled equation-of-state plot and were thus subject to rather large numerical uncertainties. The parameter b^2 was chosen equal to 2, so that $|T|$

Table I. Summary of critical behavior in the (r, θ) representation.

Critical Isochore ($\theta = 0$)	
$M = 0$	
$\left(\frac{\partial M}{\partial H}\right)_T = C_0 T^{-\gamma}$	$C_0 = a^{-1} g(0)$
$\left(\frac{\partial S}{\partial T}\right)_H = A_0 T^{-\alpha}$	$A_0 = (1-\alpha) s(0)$
Critical Isotherm ($\theta = \pm b^{-1}$)	
$\lvert M \rvert = D_\pm \lvert H \rvert^{1/\delta}$	$D_\pm = (b)^{-1} \left(\frac{b^3}{a(b^2-1)}\right)^{1/\delta} g(\pm b^{-1})$
Coexistence Curve ($\theta = \pm 1$)	
$\lvert M \rvert = B_\pm \lvert T \rvert^{\beta}$	$B_\pm = (b^2-1)^{-\beta} g(\pm 1)$
$\left(\frac{\partial M}{\partial H}\right)_T = C_\pm \lvert T \rvert^{-\gamma}$	$C_\pm = a^{-1}(b^2-1)^{\gamma}\left[\left(\frac{\beta b^2}{b^2-1} - \frac{1}{2}\right) g(\pm 1) \mp \frac{1}{2} g'(\pm 1)\right]$
$\left(\frac{\partial S}{\partial T}\right)_H = A_\pm \lvert T \rvert^{-\alpha}$	$A_\pm = -(1-\alpha)(b^2-1)^{\alpha-1} s(\pm 1)$

$= r$ on both the critical isochore and the coexistence curve. We chose a equal to B/C_0, that is, from the constants for the coexistence curve and the critical-isochore susceptibility for $T > 0$. In this way the tangent of $m(\theta)$ at $\theta = 0$ automatically passes through the point $m(1)$ at $\theta = 1$, i.e., $g(0) = g(1)$. Thus we took $T = r(1-2\theta^2)$. In (a) our choice of a gave $H = 1.1 r^{1.58} \theta(1-\theta^2)$, and in (b) $H = 58 r^{1.75} \theta(1-\theta^2)$ using the experimental values of β and δ. A simple computer program was devised to obtain values θ and $m(\theta)$ from the scaled field, $H/|T|^{\beta}$.

The striking result we have found, with this particular transformation, is that $m(\theta)$ is very nearly linear in θ to within the scatter of the experimental points. The result for the ferromagnet is shown in Fig. 2 of the paper of Ho and Litster. Here we find $g = 1.24 \pm 0.04$ where the error denotes the maximum deviation from the mean value. For the fluid data, we find $g = 1.85 \pm 0.15$. The values of g agree with the constants defining the coexistence curve [see Table I; if $b^2 = 2$ then $g(1) = B$].

We present this result, the linearity of $m(\theta)$ in these two examples, as an empirical observation. If it is confirmed in the fluid by more careful computation and found in other systems then it is clearly of considerable significance in the understanding of critical phenomena. First, it implies that the thermodynamics of the critical region can be described by the indicial parameters β and δ together with two of the parameters B, C_0, and D and possibly also A_0 or $A_\pm$. Secondly, it indicates a relationship between the temperature dependence and the field (chemical potential) dependence requiring a theoretical explanation. The consequences of a linear $m(\theta)$ and more detailed discussion of the transformation will be presented elsewhere.

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