CORRELATION BETWEEN CRITICAL COEFFICIENTS AND CRITICAL EXPONENTS

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We examine the application of a parametric equation of state to several magnetic and fluid systems near the critical point. An attractively simple form represents the experimental data very closely and this suggests there may be a functional relationship between the critical exponents and coefficients.

In a recent Letter,[1] a parametric representation of the thermodynamic functions in the neighborhood of a critical point was proposed in terms of variables r and θ. The parameter r represents a "distance" from the critical point and θ a distance around lines of constant r from one side of the coexistence curve to the other. The transformation to these variables has the property that if the scaling laws[2] hold then any thermodynamic property $\Phi(r,\theta)$ can be represented asymptotically by $r^{-x}\varphi(\theta)$, the index x giving the order of the critical singularity. In a magnetic system, one has therefore

$$H=r^{\beta\delta}h(\theta),\quad T=rt(\theta),\quad M=r^{\beta}m(\theta),$$

where T is measured from the critical temperature. The function $h(\theta)$ must be zero on the critical isochore and along the coexistence curve and $t(\theta)$ is zero along the critical isotherm. It then follows [see Eqs. (6) and (7) of Ref. 1] that the critical part of the free energy is given by (S is the difference between the entropy and the critical entropy)

$$\pi=\frac{\delta}{\delta+1}HM+\frac{1}{\beta(\delta+1)}TS=r^{\beta(\delta+1)}p(\theta).$$

This transformation with simple functions for $h(\theta)$ and $t(\theta)$ was applied to chromium tribromide[3] and it was found that $m(\theta)$ was very nearly linear in θ, with a small but significant deviation from linearity around the value of θ corresponding to $T=0$.

The purpose of this communication is to show how by a better choice of parameters the linearity of $m(\theta)$ may be improved. This optimum choice of parameters leads to the introduction of a "linear model" in which $h(\theta)$, $t(\theta)$, and $m(\theta)$ have attractively simple forms. The equation of state in this model, apart from scale factors, is entirely determined by any two of the critical indices.

We compare the model with experimental data available for a number of systems and find surprisingly good agreement. In this model the parameter r has a simple physical interpretation, and to the extent that the model is obeyed by real systems it provides a clear insight into the relationship between various thermodynamic quantities in the critical region. We examine in detail some of these relationships predicted by our model and also compare the results with theoretical calculations for the two- and three-dimensional Ising models.

We now give the arguments that lead us to the linear model. Using the parametric approach one chooses two of $h(\theta)$, $t(\theta)$, and $m(\theta)$ and analyzes the experimental data to obtain the third function. The choice of Ref. 1 is

$$h(\theta)=a\theta(1-\theta^2),\quad t(\theta)=(1-b^2\theta^2). \tag{1}$$

The resulting equation of state is then obtained by analysis of the data to determine the function $m(\theta)$. An attractively simple equation would result if $m(\theta)$ were a linear function of θ. This is possible only if the tangent to $m(\theta)$ at $\theta=0$ passes through the point $m(1)$ at $\theta=1$. For this reason we chose $a=B(b^2-1)^{\beta}/C_0$, where the coefficients B and C_0 are defined by (see Table I of Ref. 1)

$$(\partial M/\partial H)_T=C_0T^{-\gamma}\quad(H=0,\,T>0);$$

$$M=B|T|^{\beta}\quad(H=0,\,T<0).$$

In previously applying this transform to our data we chose $b^2=2$, as this gave $|T|=r$ along both the coexistence curve and the critical isochore. The resulting $m(\theta)$ is shown in Fig. 2 of Ref. 3; $m(\theta)$ is approximately linear but departs from linearity around T_c (corresponding to $\theta^2=\frac{1}{2}$).

Clearly one may attempt to improve the linearity of $m(\theta)$ by choosing b so that $m(b^{-1})$ lies on the straight line between $m(0)$ and $m(1)$. If the critical isotherm is given by $|M| = D|H|^{1/\delta}$ this condition requires that

$$\frac{C_0 B^{\delta-1}}{D^{\delta}} = \frac{b^{(\delta-3)}}{(b^2-1)^{\gamma-1}}. \tag{2}$$

Alternatively one may require that the ratio of the susceptibilities for $H=0$ and $T \gtrless 0$ is consistent with a linear $m(\theta)$. This requires

$$\frac{C_0}{C_\pm} = \frac{2}{(b^2-1)^{\gamma-1}} \frac{1}{[1-b^2(1-2\beta)]}, \tag{3}$$

where $(\partial M/\partial H)_T = C_\pm |T|^{-\gamma}$ for $H=0$, $T<0$.

The left-hand sides of Eqs. (2) and (3) are determined by the experimental data, and the right-hand sides by the choice of b^2. The right-hand sides of both equations have minimum values when regarded as functions of b^2, and both minima occur when

$$b^2 = (\delta-3)/(\delta-1)(1-2\beta). \tag{4}$$

Using the criteria of Eqs. (2) and (3) to determine b^2 for several systems, we found that the experimental values for the left-hand sides of both equations were close to or slightly below the minimum possible value for the right-hand sides. This is shown in Table I. When the experimental coefficients do not satisfy Eqs. (2) and (3) it is not possible for $m(\theta)$ to be strictly linear. However, the best experimental data now available do not have sufficient accuracy to rule out a linear $m(\theta)$. We may regard the value of b^2 in Eq. (4) as an optimum value in the following sense: that it results in an $m(\theta)$ close to linear, also that with this value of b^2 and an assumed linear $m(\theta)$ all the thermodynamic quantities take on simple mathematical forms while the parameter r has a simple physical interpretation.

We now wish to consider the consequences of a model equation of state, which we call the "linear model." In this model, $h(\theta)$ and $t(\theta)$ are given by Eq. (1), b^2 assumes the value of Eq. (4), and $m(\theta) = g\theta$.

One of the most interesting features of this model is that, apart from scale factors, the entire equation of state is determined by two of the critical exponents. In the linear model the critical coefficients are determined by the exponents and we have

$$\frac{C_0}{C_\pm} = \frac{\gamma}{\beta}\left[\frac{1-2\beta}{2\beta}\,\frac{\gamma}{\gamma-1}\right]^{\gamma-1}, \tag{5}$$

$$\frac{C_0 B^{\delta-1}}{D^{\delta}} = \left[\frac{\gamma-2\beta}{\gamma(1-2\beta)}\right]^{(\gamma-2\beta)/2\beta} \left[\frac{1-2\beta}{2\beta}\,\frac{\gamma}{\gamma-1}\right]^{\gamma-1}. \tag{6}$$

In addition, one may obtain the ratio of specific

Table I. Comparison of experimental coefficients with predictions of the linear model.

System		$CrBr_3$[a]	Ni[b]	CO_2[c]	Xe[c]	He[c]	β-Brass[d]	3d-Ising[e]	2d-Ising[e]
β		0.368	0.375	0.350	0.350	0.359	0.301	0.312	0.125
γ		1.215	1.31	1.26	1.26	1.24	1.242	1.25(1.31)	1.75
$\delta = 1 + \gamma/\beta$		4.31	4.50	4.60	4.60	4.45	5.13	5.00(5.2)	15.0
$b^2 = \frac{(\delta-3)}{(\delta-1)(1-2\beta)}$		1.51	1.71	1.48	1.48	1.49	1.29	1.33(1.39)	1.143
$\frac{C_0}{C_\pm}$	model	3.82	3.88	4.23	4.23	4.0	5.54	5.28(5.63)	60
	expt.	3.1±0.9	2.9±1.4	4.4	4.1	3.6	5.46	5.22, 5.07, 5.17[f]	37
$\frac{C_0 B^{\delta-1}}{D^{\delta}}$	model	1.51	1.65	1.60	1.60	1.58	1.77	1.73(1.92)	9.65
	expt.	1.5±.3	1.4±0.4	1.69	1.62	1.45	—	1.81, 1.74, 1.79[f]	6.85
$\frac{A_\pm}{A_0}$	model	1.41		1.29	1.29	1.28	2.17	1.96(1.44)	1.00
	expt.	—		1.27	1.27	1.34	—	2.3, 2.15, 1.95[f]	1.00

[a] Ho and Litster, Ref. 3.

[b] Weiss and Forrer, Ref. 5.

[c] Vicentini-Missoni, Sengers, and Green, Ref. 4.

[d] Als-Nielsen, private communication.

[e] Values of B, C_0, $C_\pm$ from J. W. Essam and D. L. Hunter, J. Phys. C: Phys. Soc. (London) Proc. 1, 392 (1968); $A_\pm$, A_0 from M. E. Fisher, Rept. Progr. Phys. 30, 615 (1967); and D from D. S. Gaunt, Proc. Phys. Soc. (London) 92, 150 (1967). The two values of γ are $T \lessgtr 0$ (see Essam and Hunter).

[f] For sc, bcc, and fcc lattices, respectively.

heats in zero field,

$$\frac{A_\pm}{A_0}=4\left(\frac{\beta}{\gamma}\right)^2\left[\frac{1-2\beta}{2\beta}\,\frac{\gamma}{\gamma-1}\right]^{\gamma+2\beta}, \qquad (7)$$

where

$$C_H=A_0T^{-\alpha}\quad(H=0,\,T>0),$$
$$=A_\pm|T|^{-\alpha}\quad(H=0,\,T<0).$$

In Table I the experimental values of these ratios for a number of systems are compared with the predictions of the model. The agreement is quite good, although not perfect, and the model accounts, at least in a qualitative manner, for the variation with β and δ. The agreement appears best with the gas data as analyzed by Vicentini-Missoni, Sengers, and Green.[4] In particular the estimates of the specific-heat ratio must be regarded as a success for the model. Agreement with the susceptibility ratios for $CrBr_3$ and Ni[5] does not appear especially good, but the experimental values are extrapolated from finite-field results and are not well known. Because of the uncertainties in the experimental coefficients the criteria of Table I do not provide the best experimental test of the linear model. As a second test we plot in Fig. 1 the experimental $m(\theta)$ for He^4 obtained from the data of Roach and Douglass,[6] and in Fig. 2 show $m(\theta)$ for $CrBr_3$. The resulting plot is linear within the scatter of the data for He^4, but one can imagine very slight deviations from linearity for $CrBr_3$.

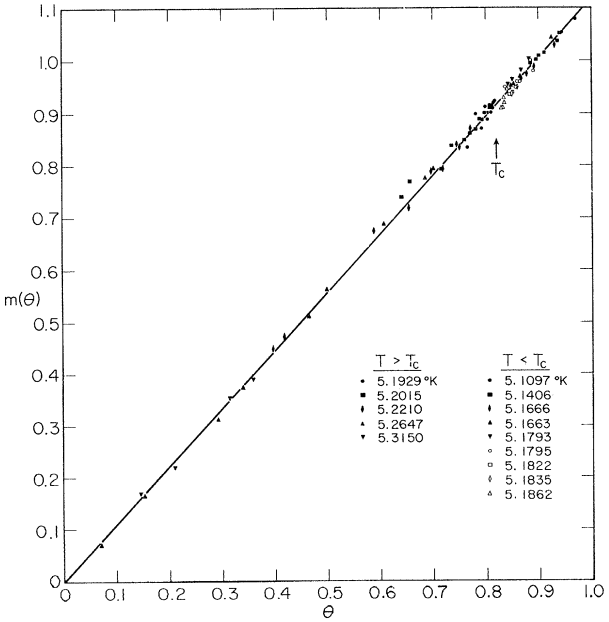

FIG. 1. A plot of $m(\theta)$ vs θ for the data of Roach and Douglass (Ref. 6). The solid line is $m=1.12\theta$.

In Table I we also compare our linear model with theoretical predictions of the Ising model. Agreement with the three-dimensional model is quite satisfactory. The predicted susceptibility ratio for the two-dimensional Ising model is well outside the limit of accuracy of the numerical estimates, and this suggests the linear model in its present form is not suitable for two-dimensional systems.

It is particularly easy to find the free energy, entropy, and susceptibility using the linear model. An interesting result is that the specific heat at constant M is independent of θ:

$$C_M=\frac{ag}{2}\beta(1-2\beta)\frac{(\delta-1)^2(\beta\delta-\beta-1)}{(\delta-3)(2-\beta\delta-\beta)}r^{\beta(\delta+1)-2}$$
$$\equiv Kr^{-\alpha}. \qquad (8)$$

In this model then, the physical significance of the parameter r is clear. Since the variable r is proportional to $C_M^{-1/\alpha}$, curves of constant r correspond to curves of constant C_M.

We also obtain a simple expression for the susceptibility,

$$\chi_T=\frac{g}{a}\left[1+\frac{2\beta\delta-3}{1-2\beta}\theta^2\right]^{-1}r^{-\gamma}. \qquad (9)$$

In the region near the critical isotherm we may eliminate r and θ from these expressions. So long as $T^2[(1-2\beta)/2\beta][g/bM]^{2/\beta}$ is small compared with unity (and this is true over a considerable portion of the critical region), the follow-

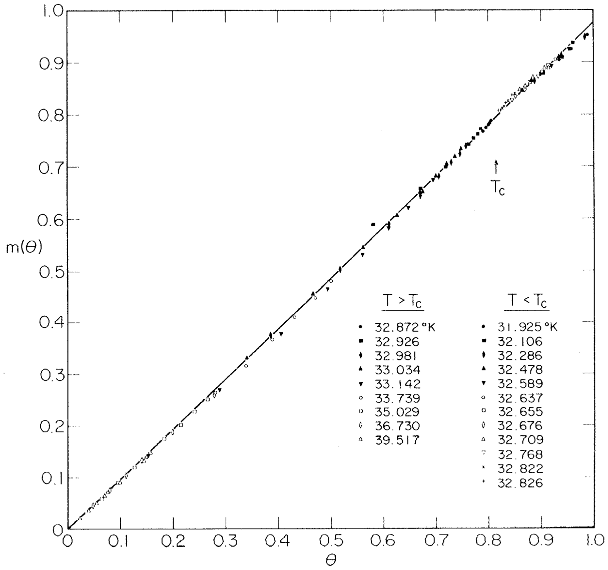

FIG. 2. A plot of $m(\theta)$ for $CrBr_3$. The line is $m=0.98\theta$.

ing simple approximate expressions are obtained:

$$\chi_T \simeq \frac{g}{2a}\,\frac{\delta-3}{\delta}\,\frac{(2\beta)^\gamma}{(\beta\delta-\beta-1)}\left\{T+\left(\frac{2b\beta M}{g}\right)^{1/\beta}\right\}^{-\gamma}, \quad (10)$$

$$C_M \simeq K(2\beta)^\alpha\left\{T+\left(\frac{2b\beta M}{g}\right)^{1/\beta}\right\}^{-\alpha}. \quad (11)$$

These expressions explain the apparent divergences (towards spinodal lines) that have been observed in finite fields for the susceptibility in $CrBr_3$[7] and the specific heat in EuS,[8] without the need to resort to complex critical temperatures.

There are many unanswered questions about a metastable region inside the coexistence curve. We may examine what our model has to say about the region for $|\theta|>1$. One might expect a metastable region inside the coexistence curve bounded by a spinodal line where the susceptibility diverges. Since $2\beta\delta>3$ for all substances we know, it is clear from Eq. (9) that χ does not become infinite inside the coexistence curve. However an examination of χ as a function of temperature along paths of constant M shows that $(\partial\chi/\partial T)_M$ diverges and that χ has a cusp when $\theta^2=(\delta-1)/(\delta-3)$. Therefore, in this sense, we have a limit of stability along a curve

$$|M|=g\left(\frac{\delta-1}{\delta-3}\right)^{1/2}\left(\frac{1-2\beta}{2\beta}\right)^\beta|T|^\beta.$$

With the classical exponents $\beta=\frac{1}{2}$, $\delta=3$, and the choice of $b^2=\frac{3}{2}$ our model correctly reproduces the metastable region of mean field theory.

The possibility of a linear $m(\theta)$ has also been examined by Cooper, Vicentini-Missoni, and Joseph,[9] who concluded that the experimental evidence was not consistent with a linear parametric equation of state. The authors of Ref. 9 analyzed coefficients obtained from a nonlinear least-squares computer fit to the experimental data of an assumed functional form for the equation of state. They generated their experimental uncertainties from the standard deviations of their computer fit. In our opinion this procedure overestimates the accuracy with which one knows the experimental coefficients. We suggest that a better procedure is to obtain $m(\theta)$ directly for each experimental point using the transform of Eq. (1) and the value of b^2 in Eq. (4). We have done this for Roach's data[6] for He^4, which are the best fluid data available. It is clear from Fig. 1 that $m(\theta)$ for helium is linear within the scatter of experimental points, although the authors of Ref. 9 conclude that "the conditions for $m(\theta)$ to be linear are violated$\cdots$ for He^4."

The very slight apparent deviations from linearity of $m(\theta)$ for $CrBr_3$ lead us to suspect that the linear model presented here does not represent the precise analytic form of the equation of state. We believe that the correct functions $h(\theta)$, $t(\theta)$, and $m(\theta)$ are closely approximated by Eqs. (1) and (4) with $m(\theta)=g\theta$. This approximation satisfactorily describes the experimental data which are presently available, and leads to an understanding of the apparent spinodal lines that have been observed.[7,8] We are also led to the interesting conclusion that there may be some functional relationship between the critical exponents and coefficients that is closely approximated by the linear model. In the absence of deeper theoretical understanding, it seems worthwhile to apply the transformation of Eqs. (1) and (4) to experimental data for comparison with the model.

In conclusion, we remark that even if the precise analytic form of our linear model is not correct, a parametric equation of state[1,10] in the critical region has several advantages. It avoids the use of power series with nonintegral exponents, and indicates the relationship of the various thermodynamic quantities to one another near the critical point when the scaling laws hold. Moreover, in the parametric form the scaling laws result from the hypothesis that $M(r,\theta)$ is a uniform function of r and θ in the critical region [i.e., that is has an asymptotic form $r^\beta m(\theta)+o(r^\beta)$ for all θ in the range -1 to $+1$]. This replaces the hypothesis of homogeneity in the usual thermodynamic variables. Expressed in terms of uniformity it becomes more transparent in what ways departures from scaling behavior can arise. For example, if $M(r,\theta)$ contained a factor $(1+r^{-x}\theta^2)^y$, then one would have different divergences in zero field for $T\gtrless 0$.

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LOW-TEMPERATURE SATURATION OF THE SUPERCONDUCTING PROPERTIES INDUCED IN SILVER BY THE PROXIMITY EFFECT*

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Critical-field measurements of silver layers sandwiched between two superconducting layers indicate that supercooling appears below a temperature T^* and that the supercooling field stays constant at low temperatures. We propose a simple theoretical model which correctly predicts the temperature of saturation as well as the observed amount of supercooling, and leads to an estimate of 0.1 for NV for silver. This model further suggests that a $1/x$ spatial dependence of the order parameter in the silver should be observed in the He^3 temperature range and below.

The proximity of a superconductor (S) may induce superconductivity in an otherwise normal metal (N). This effect has previously been studied by measurements of transition temperature, tunneling, critical current, and surface impedance. Attempts have been made to deduce from these experiments the value of the electron-electron interaction potential V, in particular to determine whether it is positive in N, which would imply that the normal metal would become an intrinsic superconductor at some lower temperature.[1,2]

The thermal conductivity also leads to information about the energy gap and the interaction potential. In contrast to tunneling and critical-current measurements, it is sensitive to electrons traveling parallel to the SN boundary so that one is not limited by problems associated with the mismatch across the boundary. We have made such measurements on PbBi/Ag/PbBi triple layers.[3] In the course of this research it turned out that a value of V can also be deduced from a study of the critical fields, and we report here on this aspect of our work.

The specimens were evaporated onto room-temperature substrates of No. 00 microscope cover glass. The thermal conductivity was measured as a function of magnetic field applied parallel to the SNS interface down to a temperature of 0.3°K. At a field below the lower critical field H_{c1} of the PbBi layers, the thermal conductivity shows a transition of the silver layer from the induced superconducting state to the normal state.

The thermal conductance of the substrate was measured in a separate run so that the conductance of the specimen could be obtained by subtraction. The measurements show that below 1.4°K and below H_{c1} the thermal conductance of the PbBi layers is negligible so that the specimen conductance is then entirely that of the silver in either its normal or its superconducting state. The normal-state Ag conductivity agrees with measurements on films of the same thickness without the PbBi layers. This agreement indicates that interdiffusion does not have any deleterious effect on our specimens.

In increasing fields the thermal conductivity of the silver reaches its normal value at some field H_s; in decreasing fields superconductivity nucleates at a field H_n. At high temperatures the two fields are equal, but below a temperature T^* the two fields separate with H_n less than H_s, indicating that H_n is a supercooling field and that the field transition is of first order. Below T^*, H_n is proportional to temperature down to a temperature T_s below which it stays constant.

Figure 1 shows the behavior of a film of 2000-Å Ag between two 2000-Å layers of PbBi. A second specimen of similar composition was measured at 0.6°K. The fields H_n and H_s were about 12% larger, but the ratio H_n/H_s (which is used in the subsequent analysis) was within 3% of the