Scaled-equation-of-state analysis of the specific heat in fluids and magnets near critical point

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Scaled equations of state for fluids and magnets are studied near the critical point, with particular emphasis on specific-heat predictions. The importance of fitting both the exponent and the critical amplitudes is emphasized. Previous proposals, such as the Missoni, Levelt Sengers, and Green (MLSG) and "linear-model" equations are examined, and the corresponding amplitude ratio A/A' calculated as a function of the parameters. The linear model is found to be inapplicable to Heisenberg-like systems in which the exponent α is negative, and $A/A' > 1$. Specific-heat data on Xe, CO_2, Ni, and EuO are compared to predictions based on the MLSG and linear-model equations, with parameters previously determined using pressure, volume, and temperature (*PVT*) and magnetization, field, and temperature (*MHT*) data. There is a small but probably significant discrepancy for the fluids, and a large deviation in the magnetic case. A "modified MLSG" equation is proposed, with an additional parameter, by means of which both *PVT* (*MHT*) and specific-heat data may be fitted. Using this equation, an estimate is made for the effect of small fields on rounding the specifc-heat singularity in magnetic systems. In EuO it is found that a field as small as the earth's field has a perceptible effect on the specific heat rounding near T_c.

I. INTRODUCTION

A great deal of effort has been directed in recent years toward analyses of thermodynamic data on magnets and fluids near the critical point, in terms of scaled equations of state.[1-4] For the most part, the data involved pressure, volume, and temperature (*PVT*) or magnetization, field, and temperature (*MHT*) measurements, and the general conclusion drawn from that work[1-4] was that simple equations with a small number of parameters gave a satisfactory fit over the whole thermodynamic plane. The purpose of the present paper is to bring the results of these analyses to bear on specific-heat data, and in this way to provide a sensitive test of the previously proposed equations of state. Our general conclusion will be that specific-heat information is sufficient to rule out many proposals which have been claimed to be consistent with existing *PVT* or *MHT* data. In particular, the "linear-model"[5] equation of state shows large deviations for magnetic systems, and smaller, but possibly significant ones, for fluids. The equation originally proposed by Missoni, Levelt Sengers, and Green (MLSG equation),[1] which has more flexibility, can be made to fit specific-heat data on fluids and magnets, but with parameter values which may be rather far from the "best-fit" values obtained from *PVT* and *MHT* measurements. We show, however, that a simple modification of the MLSG equation, which involves an extra parameter, leads to an improved fit for both fluids and magnets.

The task of determining the equation of state of a substance near the critical point can be approached from two points of view. The first and more fundamental one attempts to find the true asymptotic behavior, which is presumably identical for all members of a universality class.[6] In this approach it is important to take into account all relevant theoretical information, and to modify the analysis whenever theoretical advances occur. For example, it is known that the true equation of state satisfies certain stringent analyticity requirements, and these preclude the use of many simple scaling expressions, for arbitrary values of the exponents.[7] Another theoretical insight which must be brought to bear on the analysis is the strong evidence[8-11] that there exist nonanalytic corrections to the leading power laws which characterize the critical singularities, even in the simplest systems (e.g., the Ising model). These singular correction terms must be included in a rigorous formulation, and the consequent increase in unknown parameters makes such an analysis extremely difficult.

In view of these difficulties, it is reasonable to adopt a second, more empirical point of view, and to search for an equation of state which will fit the best existing experimental data to within their statisitical accuracy, without necessarily satisfying all known theoretical conditions. This approach has led to the development of a number of empirical proposals[1,5] which contain only a small number of parameters, and satisfy the scaling and homogeneity relations[7] which are expected to hold for the exact equations. The virtue of such empirical equations of state is their relative mathematical simplicity, and their widespread applicability, with parameters which do not change significantly from one substance to the next. Such a numerically accurate representation of a vast amount of data is extremely useful in practice, and has for example been applied to a calculation of gravity corrections in a fluid near the critical point.[12-14] Similarly it can be used to predict the specific heat of a ferromagnet in finite field, which is one of the motivations for the present work.

As experimental and theoretical techniques improve, the two approaches outlined above should begin to merge, but there are at present many open questions left, which prevent a straightforward application of the theory to an analysis of experiment. Perhaps the most important difficulty is the apparent discrepancy between the critical exponents of fluids and of the Ising model, which has recently been reemphasized by Levelt Sengers.[3] Although we believe that the discrepancy may still be resolved by an increase in the errors in both the theory and the experimental analysis, we must recognize that the difference in exponents is as large as that between the various universality classes (Ising, X-Y, Heisenberg) in three dimensions. As a result we cannot, at this stage, apply our theoretical knowledge of the Ising equation of state[15,16] to real fluids with great confidence.

In the present paper we adopt primarily the empirical point of view, with a shift of emphasis to the specific heat. We compare existing specific-heat data to equations of state whose parameters were previously determined. Emphasis is placed, in the analysis, on the distinction between "universal" quantities (such as the exponent α or the critical ratio A/A') and nonuniversal ones, such as the amplitude A itself. The former quantities are more important from a theoretical standpoint,[16] but the latter are also predicted by the analysis, and their correctness is an important test of thermodynamic consistency. In practice, the universal and nonuniversal parameters are strongly correlated in the empirical fits,[4] so that the two types of quantities cannot be treated on entirely different footing. Nevertheless, we believe that it is inadvisable to adjust an exponent, for example, in order to obtain a better fit to an amplitude, which is not universal.

In our opinion, the ideal strategy for finding the correct equation of state would proceed in the following manner: First, the critical exponents and amplitudes are determined by analyzing data along selected thermodynamic paths (the critical isochore, the coexistence curve, etc.), with T_c and ρ_c treated as adjustable parameters (consistent between different sets of data), and the scaling relations imposed on the exponents. (These constraints may already be impossible to satisfy without singular correction terms.) Then the universal part of the equation of state is obtained by fitting to critical ratios (see Sec. II) which are supposed to be universal.[6] By this procedure the complete equation of state is specified, and it may be tested by comparing to data along other paths. If the fit is deemed unsatisfactory within the statistical accuracy of the analysis, then it must be concluded that the original assumptions concerning the critical exponents and correction terms were incorrect, and these must be modified. Alternatively, the equation of state might be at fault, and additional universal parameters must be introduced. Clearly, such an analysis is only meaningful if a large amount of reliable experimental information is available, and in practice a less complete procedure must be followed.

We have found that neither the linear model[5] nor the MLSG equations[1] yields a completely satisfactory fit to existing specific-heat data along the critical isochore and coexistence curve of fluids and Heisenberg-like magnetic systems (Xe, CO_2, EuO, Ni), the discrepancy being much more significant in the magnetic case. On the other hand, a simple modification of the MLSG equation, which contains one additional universal parameter, is sufficient to fit the specific heat in these systems, within the accuracy of the measurements.

In Sec. II the "scaling"[7,17] and "parametric"[18] representations for the equation of state are reviewed, and universal variables introduced. Section III discusses the specific heat, both at zero field ($\rho=\rho_c$), where the amplitudes A and A' are calculated, and at finite field. The magnitude of the "rounding" effect due to small fields (e.g., the earth's field) is estimated for various systems. Specific equations of state are considered, such as the linear model and MLSG equation, and it is shown that they predict values for A/A' which in general differ from the best experimental and theoretical estimates. A "modified MLSG" equation is introduced, with an additional parameter, which may be used to fit the desired value of A/A'. In Sec. IV a number of specific systems are considered, such as CO_2, Xe, EuO, Ni, FeF_2, $RbMnF_3$, the ^{4}He λ point, and the Ising model. Data on the specific heat of these systems are compared with values calculated on the basis of the various approximate equations of state. For Ni and EuO the specific heat is calculated at finite field, and compared with experimental data. Several detailed calculations are summarized in the Appendixes.

II. UNIVERSAL AND NONUNIVERSAL QUANTITIES

Near an ordinary critical point the equation of state is described in terms of two independent variables, for example the temperature T and the density ρ for a fluid or the magnetization M for a magnet. This is usually written as

$$\mu = \mu(\rho, T) \tag{2.1a}$$

or

$$H = H(M, T) , \tag{2.1b}$$

where μ is the chemical potential and H the magnetic field. (The analogy between fluids and magnets is well known[7] and we shall use both notations interchangeably.) According to the scaling hypothesis,[17,7] when one is sufficiently close to the critical point this function of two variables may be expressed in terms of critical exponents and a function of one variable,

$$\mu - \mu(\rho_c, T) \equiv \Delta\mu = \Delta\rho \,|\Delta\rho|^{\delta-1} h(x) , \tag{2.2a}$$

$$H = M|M|^{\delta-1} h(x) , \tag{2.2b}$$

where

$$x \equiv t|\Delta\rho|^{-1/\beta} = t|M|^{-1/\beta} , \tag{2.3}$$

$$\Delta\rho \equiv \rho - \rho_c , \tag{2.4}$$

$$t \equiv (T - T_c)/T_c . \tag{2.5}$$

(We are using the standard notation,[7] which is defined more precisely in Appendix A.) The function $h(x)$ must satisfy a certain number of conditions[7] in order to ensure analyticity of $\mu(\rho, T)$ and $H(M, T)$ in the one-phase region.

The hypothesis of universality[6] states that all systems possessing critical points are divided up into equivalence classes, within which the critical exponents have specified values. These classes are determined by general features of the Hamiltonian, such as symmetry and dimensionality. It is expected,[6,16] moreover, that in addition to the critical exponents, the function $h(x)$ will also be universal (i.e., invariant within each equivalence class), for a suitable choice of scale factors for ρ and μ (M and H). This means that one may define nonuniversal constants x_0 and h_0 for each system, such that the function

$$\tilde{h}(\tilde{x}) = \tilde{h}(x/x_0) \equiv h_0^{-1} h(x) \tag{2.6}$$

is the same for all systems within a universality class. In pracitce, it is convenient to choose x_0 and h_0 such that

$$\tilde{h}(\tilde{x} = -1) = 0 , \tag{2.7}$$

$$\tilde{h}(\tilde{x} = 0) = 1 . \tag{2.8}$$

We shall henceforth refer to $\tilde{h}$ and $\tilde{x}$ as "universal variables." The universality of $\tilde{h}(\tilde{x})$ of course implies the universality of the critical exponents, but there are also conditions on the critical amplitudes. In particular, certain ratios of amplitudes along the different paths in the thermodynamic plane, which are independent of the scale factors x_0 and h_0, must also be universal. From an experimental point of view, the most important ones are the critical ratios[19] Γ/Γ', A/A', and $D\Gamma B^{\delta-1}$, where Γ, Γ', A, A', D, and B are the usual amplitudes for the susceptibility, specific heat (above and below T_c on the critical isochore), critical isotherm, and coexistence curve (see Appendix A).

Usually, the function $\tilde{h}(\tilde{x})$ is determined from experiment by fitting a few parameters, e.g., two critical exponents and a shape parameter such as b^2 or E_2 (see Sec. III). It is then a nontrivial check of the correctness of the assumed equation of state and exponent choices to verify that the ratios Γ/Γ', A/A', and $D\Gamma B^{\delta-1}$ obtained from $\tilde{h}(\tilde{x})$ agree with experiment. The representation of the equation of state in terms of $h(x)$ will be referred to as the "scaling representation."[7] There also exists a "parametric representation,"[18] defined in Appendix E, in which there are other scaling constants corresponding to x_0 and h_0 (they are denoted by k and a). It is clear from the formulas of Appendix E that the critical ratios are independent of these scaling constants.

In order to determine the scale factors x_0 and h_0 it is sufficient to measure two critical amplitudes, for example B and Γ, Eqs. (A1) and (A2). The scale factors are then given in terms of $\tilde{h}(\tilde{x})$, B, and Γ, by

$$x_0 = B^{-1/\beta} , \tag{2.9}$$

$$h_0 = \Gamma^{-1} B^{-\gamma/\beta} \lim_{\tilde{x}\to\infty} [\tilde{x}^{\gamma}/\tilde{h}(\tilde{x})] . \tag{2.10}$$

Similar formulas exist in the parametric representation (see Appendix E). Once x_0, h_0, and $\tilde{h}(\tilde{x})$ are known, the leading singularities in all thermodynamic quantities are fully specified. In particular, the amplitudes and exponents for the specific heat may be calculated and compared with experiment. In practice, the scale of the amplitudes A and A' obtained from $h(x)$ may not agree perfectly with experiment, even if $h(x)$ [or $\tilde{h}(\tilde{x})$] yields the correct experimental value of the ratio A/A'. The correctness of A or A' separately is an important check on the thermodynamic consistency of the equation of state. Indeed, an incorrect scale factor for the specific heat is an indication either that the assumed form for $\tilde{h}(\tilde{x})$ is inadequate, or that the exponents and amplitudes obtained from a fit to the experimental data are inconsistent. Such a situation may arise when singular correction terms play an important role near the critical point, if these are not adequately taken into account.

Heisenberg and X-Y systems. It has long been suspected,[20] and has recently been confirmed by a renormalization-group calculation,[21] that the susceptibility diverges along the coexistence curve for $T<T_c$, in Heisenberg and X-Y models. This feature is not present in any of the explicit equations of state considered in this paper. In terms of the scaling representation (2.2), we may still define universal variables according to (2.7) and (2.8), but it is expected that near $\tilde{x}=-1$, $\tilde{h}(\tilde{x})$ will have the form

$$\tilde{h}(\tilde{x}) \sim (1+x)^v, \quad x \to (-1)^+ \tag{2.11}$$

for Heisenberg and X-Y systems. The exponent v is greater than unity, and is estimated[21] to be equal to $2/(d-2)$, i.e., $v=2$ in three dimensions. In the parametric representation we would have [see Eq. (E1)]

$$H \sim (1-\theta^2)^v, \quad \theta^2 \to 1^- . \tag{2.12}$$

The range of $\tilde{x}$ or θ^2 values over which Eqs. (2.11) and (2.12) are valid is not known, but it is expected[21] to be small. It may be shown from the expression (C11) for the specific heat given in Appendix C, that the nonanalytic behavior of $\tilde{h}(\tilde{x})$ does not contribute any singularity in $C_H(t,H)$ as $H\to 0$ for $T<T_c$. Thus the precise form of $\tilde{h}(\tilde{x})$ near $\tilde{x}=-1$ is probably not very important for the specific heat. (In particular, numerical calculations using the regular functions to be discussed in Sec. IV do not reveal large contributions to A' from $\tilde{x}\approx -1$.)

Experiments on Heisenberg-like systems[22-24] and numerical simulations[25] have thus far failed to reveal the expected divergence in the susceptibility, which suggests that Eq. (2.11) is only valid very near the coexistence curve, and estimates based on the ϵ expansion support this view.[21] On the other hand, it is interesting to note that the Heisenberg equation of state proposed by Milošević and Stanley[26] has $v=\frac{4}{3}$, which is smaller than the value $v=2$ of Ref. 21, but does lead to a divergent susceptibility for $T<T_c$. For real systems there are probably more-fundamental reasons why the divergence has not been observed, having to do with domains and dipolar interactions. Indeed, it is precisely for $T<T_c$ and $H\to 0$ that dipolar interactions become most important in real magnets, and these tend to cut off the divergence. In fact, it may well be that the equations of state used in this paper, with Heisenberg exponents and a non singular susceptibility for $T<T_c$, are a better representation of real ferromagnets than that of a pure Heisenberg model. Thus, since there is no experimental evidence for a singular equation of state near the coexistence curve below T_c, it is consistent, from an empirical point of view, to fit to regular functions.[22,23] On a more fundamental level, we would of course like to clarify the relationship between real materials and Heisenberg or X-Y models, but this problem, like the problem of the discrepancy between Ising and fluid exponents,[3] is outside the scope of the present work. In practice, we expect the critical ratio Γ/Γ' to be most subject to uncertainty, since it vanishes in the pure-Heisenberg or X-Y case, so we shall not attach any particular significance to our predictions for this quantity.

III. AMPLITUDE RATIO A/A' AND THE FIELD DEPENDENCE OF THE SPECIFIC HEAT

A. Theoretical predictions for A/A'

Let us first review what is known theoretically about the amplitude ratio A/A'. In his original work on the scaling hypothesis, Widom[17] considered the limit $\alpha\to 0$, and proved that scaling implies $A=A'$ in that case. More recently, Brezin *et al.*[27] have calculated the amplitude ratio for an n-vector model using the ϵ expansion ($\epsilon=d-4$), and found

$$\frac{A}{A'}=2^{\alpha}\frac{n}{4}(1+\epsilon)+O(\epsilon^2) . \tag{3.1}$$

This expression may also be rewritten in a form which emphasizes the behavior for $\alpha\to 0$, namely,

$$\frac{A}{A'}=1-\frac{\alpha(n+8)}{2\epsilon}\left[1+\left(\frac{n^2+4n+28}{2(n+8)^2}\right)\epsilon\right] + \alpha\ln 2+O(\epsilon^2) , \tag{3.2}$$

since[16,28]

$$\alpha=\left(\frac{(4-n)}{2(n+8)}\right)\epsilon-\left(\frac{(n+2)^2(n+28)}{4(n+8)^3}\right)\epsilon^2+O(\epsilon^3) . \tag{3.3}$$

In order to obtain an estimate for three dimensions, one must extrapolate Eqs. (3.1) and (3.2) to $\epsilon=1$. The most straightforward way is to expand the factor 2^{α} in Eq. (3.1) and only keep the linear term in ϵ, i.e.,

$$A/A'=\tfrac{1}{4}n\{1+\epsilon[1+\tfrac{1}{2}(\ln 2)(n-4)/(n+8)]\} . \tag{3.1'}$$

The results are shown in Table I, for different values of n.

Alternatively, one can use Eq. (3.2) to determine the parameter

$$\mathcal{P}\equiv \alpha^{-1}(1-A/A') , \tag{3.4}$$

which experimentally seems to be a smooth function of α (see below). In particular, for the logarithmic case $\alpha\to 0$, $\mathcal{P}$ goes to a finite limit[7] which is equal to

$$\mathcal{P}=\Delta C/A , \tag{3.5}$$

where the specific heat is written as

$$C=-A\ln|t|,\quad t>0 \tag{3.6a}$$

$$C=-A\ln|t|+\Delta C,\quad t<0\ . \tag{3.6b}$$

The regularity of $\mathcal{P}$ for widely different systems was first pointed out by Voronel' *et al.*,[29(a)] on the basis of an analysis of experiments in terms of logarithmic singularities. From Eq. (3.2) we find

$$\mathcal{P}=\left(\frac{n+8}{2\epsilon}\right)\left[1+\left(\frac{n^2+4n+28}{2(n+8)^2}\right)\epsilon\right]-\ln 2+O(\epsilon^2)\ . \tag{3.7}$$

This form for $\mathcal{P}$ is designed to yield a reasonable extrapolation to the range $\epsilon\approx 1\gg\alpha$. Values of $\mathcal{P}$ obtained from Eq. (3.7) for $\epsilon=1$ and various n are also shown in Table I. Needless to say, these methods of extrapolation involve large uncertainties, but their mutual consistency, and the agreement with experimental values to be discussed below, lend some support to our procedure.

The only system for which A/A' has been obtained from series expansions is the Ising model,[30] where even the scaling result $\alpha=\alpha'$ was not obtained unambiguously. Nevertheless, by imposing the symmetry relation $\alpha=\alpha'$, Gaunt and Domb[30] found a ratio

$$A/A'=0.75 \tag{3.8}$$

which does not agree with the value obtained from the ϵ expansion in Table I. The value of $\mathcal{P}$ [Eq. (3.4)] for this case,[30] with $\alpha=\frac{1}{8}$, is $\mathcal{P}=2$, which is again rather far from our expectations based on the ϵ expansion (Table I) and experiment (see below). We believe the value in Eq. (3.8) to be incorrect, as a result of the inaccuracy of the low-temperature series. We shall show in what follows that the Ising value is likely to be $A/A'\approx 0.5$, but a more accurate determination is highly desirable.

B. Experimental results

Ahlers,[11] and Ahlers and Kornblit[31] have recently discussed the trends in experimental values of A/A' and α for different systems. They found that the amplitude ratio could be determined with relatively high precision from the data, provided adequate attention was paid to the form of corrections to the leading powers. Let us write the specific heat as

$$C=(A/\alpha)t^{-\alpha}(1+Dt^{x})+B_0,\quad t>0 \tag{3.9a}$$

$$C=(A'/\alpha)(-t)^{-\alpha}[1+D(-t)^{x'}]+B_0',\quad t<0. \tag{3.9b}$$

The existence of a singular correction term such as in Eqs. (3.9a) and (3.9b) was first demonstrated experimentally by Greywall and Ahlers[10] for the superfluid density of ^{4}He. It is expected theoretically[8,9] that in the case of the specific heat, $B_0=B_0'$, and that $x=x'\approx 0.5\pm 0.2$. Indeed, a value $B_0\neq B_0'$ would correspond to a correction exponent $x=x'=\alpha$, which is much smaller than expected. For $\alpha<0$, in fact, one must have $B_0=B_0'$, since a discontinuity at T_c corresponds to $\alpha=0$, which would dominate a negative α. In analyzing experimental data one frequently uses the simplified expressions

$$C=(A/\alpha)t^{-\alpha}+B_0,\quad t>0 \tag{3.9c}$$

TABLE I. Theoretical estimates of α, A/A', $\mathcal{P}$, and Q.

System	n	α	A/A'	$\mathcal{P}$	Q	Method	Reference
Ising	1	0.08 [a]	0.53 [b]	4.72 [c]	0	ϵ expansion	28
X-Y	2	−0.02 [a]	1.03 [b]	5.30 [c]	0	ϵ expansion	28
Heisenberg	3	−0.10 [a]	1.52 [b]	5.92 [c]	0	ϵ expansion	28
Ising $S=\frac{1}{2}$	1	0.125	0.75	2	7.3	Series	30
X-Y ($S=\infty$)	2	-0.02 ± 0.03	⋯	⋯	⋯	Series	d
Heisenberg ($S=\infty$)	3	-0.14 ± 0.06	⋯	⋯	⋯	Series	e
Heisenberg ($S=\infty$)	3	−0.09	⋯	⋯	⋯	Series	f
Ising $S=\frac{1}{2}$	1	0.125	0.51	3.9	0	Eq. of state	g
Heisenberg $S=\frac{1}{2}$	3	−0.198	2.64	8.3	0	Eq. of state	32
Heisenberg $S=\infty$	3	−0.13	1.46	3.5	0	Eq. of state	32

[a] From Eq. (3.1′) with $\epsilon=1$.
[b] From Eq. (3.1) with $\epsilon=1$.
[c] From Eq. (3.4) with $\epsilon=1$.
[d] M. Ferer *et al.*, Phys. Rev. B 8, 5205 (1973).
[e] M. Ferer *et al.*, Phys. Rev. B 4, 3954 (1971).
[f] D. S. Ritchie and M. E. Fisher, Phys. Rev. B 5, 2668 (1971).
[g] Reference 15 and this work.

$$C = (A'/\alpha)(-t)^{-\alpha} + B_0, \quad t<0 \qquad (3.9d)$$

since the correction terms are difficult to determine. In general, one may define the parameter

$$Q \equiv A^{-1}(B_0 - B_0'), \qquad (3.10)$$

which is a measure of the "jump" in specific heat at the transition. According to the previous discussion, the parameter Q should be identically zero, unless one is dealing with a logarithmic singularity ($\alpha = 0$), in which case Q is just equal to the parameter $\mathcal{P}$ [Eq. (3.5)]. (In mean-field theory we have $B_0 \neq B_0'$, but $A = A' = 0$.) For $\alpha \neq 0$, we expect the leading singularity to be reflected in the value of $\mathcal{P}$ [Eq. (3.4)], and a fit which includes a finite value of Q has the singularity shared between the leading term and the jump, so that the exponent α is not meaningful.

A summary of selected experimental results on α, A/A', $\mathcal{P}$, and Q is presented in Table II. Generally speaking, it is seen that in those cases where Q is either zero or small, the values of α, A/A', and $\mathcal{P}$ are quite consistent with theoretical expectations (cf. Table I), and in particular $\mathcal{P}$ varies relatively little from system to system. On the other hand, the most irregular values of $\mathcal{P}$ are associated with large values of Q, which we believe to be incorrect. We shall thus prefer those analyses which impose the condition $Q = 0$, when it is statistically allowed by the data. (We shall see an example in Sec. IV, in the analysis of CO_2, when this does not seem to be the case.) Having imposed this condition, we find rather good agreement between experiment and theory for A/A' and $\mathcal{P}$, and it is thus reasonable to test an equation of state by its ability to fit the experimental A/A'.

C. Calculation using the "linear model"

Let us now investigate the prediction of the linear model for the ratio A/A'. In particular, we wish to see how this ratio depends on the other (universal) parameters in the model,[29(b)] namely, the critical exponents and b^2. We shall let the expo-

TABLE II. Experimental estimates of α, A/A', $\mathcal{P}$, Q, D, D', and x. $C = (A/\alpha)t^{-\alpha}(1+Dt^x) + B_0$, $t>0$, $\mathcal{P} = \alpha^{-1}(1 - A/A')$, $C = (A'/\alpha)(-t)^{-\alpha}[1 + D'(-t)^x] + B_0'$, $t<0$, $Q = A^{-1}(B_0 - B_0')$.

System	n	α	A/A'	$\mathcal{P}$	D [a]	D' [a]	x	Q [a]	Reference
CO_2	1	0.125	0.53	3.7	0	0	···	−6.2	36
CO_2	1	0.095	0.54	4.9	0	0	···	0	This work
Xe	1	0.125	0.63	2.9	0	0	···	−0.8	35
Xe	1	0.11	0.44	5.1	0	0	···	0	This work
Ar	1	0.12	0.52	4.0	0	0	···	−0.5	b
Ethane	1	0.12	0.54	3.8	0	0	···	−0.6	b
^{3}He	1	0.105	0.44	5.3	0	0	···	0	c
Methanol-cyclohexane	1	0.125	0.48	4.2	0	0	···	−1.2	d
FeF_2	1	0.16	0.53	2.9	0	0	···	−3.6	43
FeF_2	1	0.135	0.49	3.8	0	0	···	0	e
^{4}He λ point	2	−0.015	1.06	4.2	−0.04	0.01	0.5	0	f
EuO ($\lvert t\rvert < 0.02$)	3 [g]	−0.026	2.0	40	0	0	···	−4.4	44
EuO ($\lvert t\rvert > 0.02$)	3 [g]	−0.09	1.0	0	0	0	···	−2.9	44
EuO	3 [g]	−0.044	1.22	5.0	0	0	···	0	40
EuO	3 [g]	−0.1	1.51	5.3	−0.2	−0.1	0.6	0	40
Fe	3	−0.12	1.04	0.3	0	0	···	−1.5	h
Fe	3	−0.103	1.41	3.9	0	0	···	0	31
Ni	3	−0.10	1.14	1.4	0	0	···	1.4	39
Ni	3	−0.089	1.26	3.0	0	0	···	−0.6	h
Ni	3	−0.091	1.40	4.4	0	0	···	0	31
$RbMnF_3$	3	−0.135	1.46	3.4	0	0	···	0	31

[a] The value zero for this parameter, when it occurs, was imposed in the fit.

[b] A. V. Voronel, V. G. Gorbunova, V. A. Smirnov, N. G. Shmakov, and V. V. Shchekochikhina, Zh. Eksp. Teor. Fiz. 63, 964 (1972) [Sov. Phys.—JETP 36, 505 (1973)].

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[f] G. Ahlers (private communication).

[g] Dipolar effects expected.

[h] F. L. Lederman, M. B. Salamon, and L. W. Shacklette, Phys. Rev. B 4, 2981 (1974).

nents range over the values expected for Ising, X-Y, and Heisenberg systems ($-0.15 < \alpha < 0.15$). As mentioned in Sec. II, the fact that the linear model yields a finite susceptibility on the coexistence curve should not in itself exclude its applicability to X-Y or Heisenberg-like systems, so long as a numerically accurate fit can be made to *PVT* or *MHT* data. In fact, even for Ising systems it has been argued convincingly by Gaunt and Domb[15] that the linear model is not correct in two and three dimensions, and it fails in order ϵ^2 in the ϵ expansion.[16] Nonetheless, for proper choices of the parameter b^2, the equation of state can be fit reasonably well by the linear model, for both Ising and Heisenberg systems,[16] as well as for real fluids and magnets,[4,5,22,23] and it is reasonable to ask whether the specific heat will also agree.

The results for A/A', calculated from Eqs. (E18) and (E19), as a function of α, β, and b^2 are shown in Figs. 1–3. It is seen in Fig. 2, for example, that for $\beta = 0.355$ it is only in the vicinity of $\alpha = 0.08$ that there is any value of b^2 for which A/A' can be made to agree with the expected values (solid points), obtained from Tables I and II. The important feature of the linear model revealed in Figs. 1 and 2 is an apparently spurious minimum (or maximum) value that A/A' can attain for given values of the exponents, as b^2 is varied. In Fig. 3, we show similar curves using the Ising value $\beta = 0.3125$. This low β leads to a larger region, $0.07 \lesssim \alpha \lesssim 0.12$, for possible agreement between the linear-model A/A' and its expected value for Ising-like systems. However, such a low β value appears not to be warranted by experiments in fluids.[3,29(b)] For the Heisenberg case, the necessary adjustment in the exponent β is far beyond the allowable range of uncertainty. Indeed, to obtain $A/A' \approx 1.5$ in the linear model for $\alpha \sim -0.14$ one would need $\beta < 0.28$. Although this result could be interpreted merely to confirm the inapplicability of the linear model to the Heisenberg system, we interpret it to indicate a basic flaw in this equation, even for use as a purely empirical tool. The linear model has a built-in restriction on A/A' which is very likely to be spurious, and which limits the flexibility of the equations. It happens that A/A' can be made to fit[14] the experimental $A/A' \approx 0.5$ on Ising systems of fluids, for $\alpha = 0.08$ and $\beta = 0.355$, or for $\alpha = 0.11$ and $\beta = 0.3125$ (Figs. 2 and 3), but if the values $\alpha = 0.125, \beta = 0.355$ (for fluids[4]) or $\alpha = 0.125, \beta = 0.3125$ (for the Ising model[15]) are chosen, then we find $A/A' < 0.4$, and

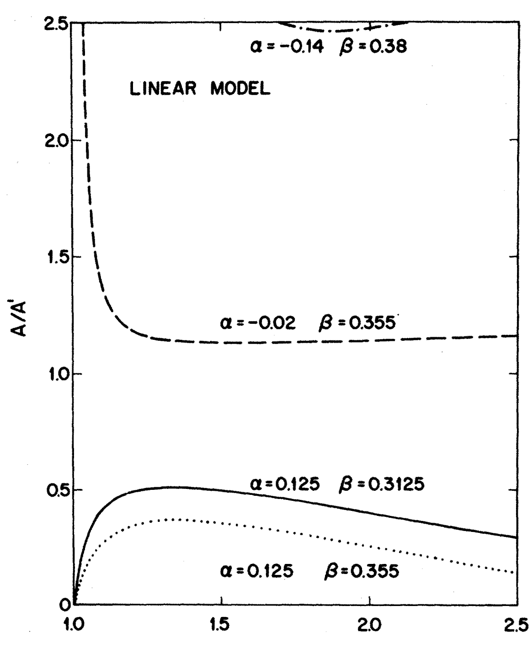

FIG. 1. Amplitude ratio A/A' for the specific heat as a function of the linear-model parameter b^2. The curves correspond to representative values of the critical exponents α and β for the following systems: dotted lines, fluids; solid line, Ising; dashed line, X-Y; and dash-dot line, Heisenberg. For each set of exponents, the ratio A/A' reaches a maximum or minimum value as b^2 is varied.

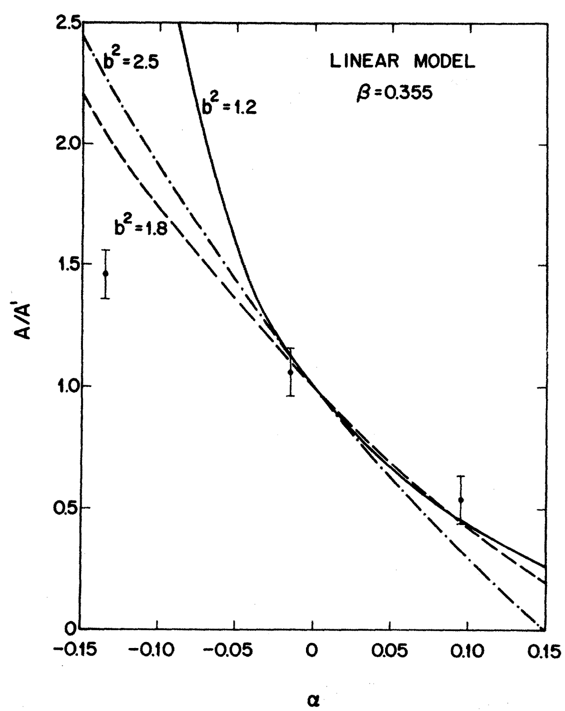

FIG. 2. Amplitude ratio A/A' as a function of α for the linear model. Experimentally determined A/A' ratios are also plotted, with error bars, for the systems CO_2 ($n = 1$, $\alpha = 0.095$), ^{4}He λ point ($n = 2$, $\alpha = 0.015$), and $RbMnF_3$ ($n = 3$, $\alpha = -0.135$); see Table II. For $\alpha < 0$, a minimum ratio A/A' is attained for $b^2 \simeq 1.8$.

$A/A' < 0.51$, respectively (see Fig. 1). In any case, we do not believe that the critical exponents should be treated as adjustable parameters to take care of discrepancies in A/A'. For Heisenberg and X-Y systems, which have negative α,[11] Fig. 1 shows that A/A' has a minimum when b^2 varies, and one would have to choose extremely unrealistic values of β to fit the observed A/A'.

D. Calculations using the MLSG equation

Formulas for the specific heat in terms of the scaling representation have been obtained by Griffiths,[7] and are reproduced in Appendix C. It should be noted that whereas Griffiths restricted his discussion to $\alpha \geq 0$, the generalization to $\alpha < 0$ may be made quite simply by replacing Eq. (22) of Griffiths, which reads

$$a(x) = \beta\left(\frac{h_0}{2-\alpha} + \frac{h_1 x}{1-\alpha} - x|x|^{1-\alpha}\int_0^x dy\, |y|^{\alpha-3}[h(y) - h_0 - h_1 y]\right), \tag{3.11}$$

by the equation

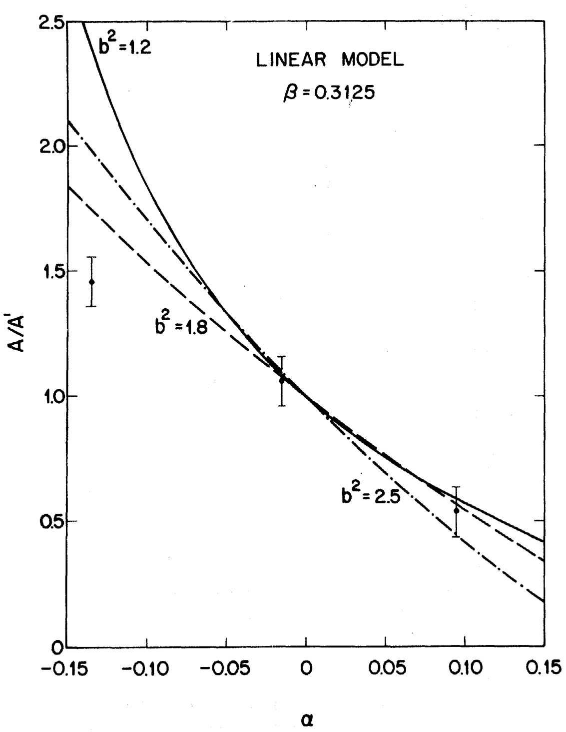

FIG. 3. Amplitude ratio A/A' as a function of α for the linear model, for $\beta = 0.3125$. This value of β leads to an improved agreement with the experimental ratios.

$$a(x) = \beta\left(\frac{h_0}{2-\alpha} + \frac{h_1 x}{1-\alpha} + \frac{h_2 x^2}{-\alpha} - x|x|^{1-\alpha}\int_0^x dy\, |y|^{\alpha-3}[h(y) - h_0 - h_1 y - h_2 y^2]\right). \tag{3.12}$$

It is easy to show that expressions (3.11) and (3.12) are equivalent for $\alpha > 0$, but Eq. (3.12) removes the divergence which occurs in (3.11) at $y = 0$ for $\alpha < 0$. [We shall not consider the logarithmic case ($\alpha = 0$) explicitly.] The formulas for the specific heat are given in Appendix C, Eqs. (C9)–(C13).

A rather simple explicit form for $h(x)$ which has been widely used is the "MLSG equation,"[1] which is written in the form

$$h(x) = E_1\left(\frac{x+x_0}{x_0}\right)\left[1 + E_2\left(\frac{x+x_0}{x_0}\right)^{2\beta}\right]^{(\gamma-1)/2\beta}, \tag{3.13}$$

or in "universal variables," in the form

$$\tilde{h}(\tilde{x}) = (1+E_2)^{-(\gamma-1)/2\beta}(1+\tilde{x})[1 + E_2(1+\tilde{x})^{2\beta}]^{(\gamma-1)/2\beta}. \tag{3.14}$$

It is seen that the only parameters in Eq. (3.14) are two critical exponents (β and $\alpha = 2 - 2\beta - \gamma$), and E_2. The integration necessary to obtain A and A' from Eq. (3.14) was performed numerically, for given values of α, β, and E_2. Details are given in Appendix D. The results are shown in Figs. 4 and 5, where it is seen that the values of A/A' obtained span a much broader range than in the linear model. Thus for reasonable values of α and β a value of E_2 can be found to fit the experimental value of A/A'. Of course it is not clear

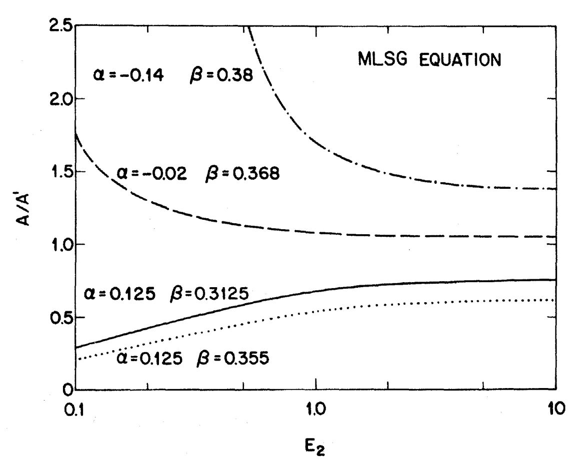

FIG. 4. Amplitude ratio A/A' as a function of the parameter E_2 in the MLSG equation. The sets of exponents α and β represent typical values for the different universality classes.

a priori that the same value of E_2 will also fit Γ/Γ' or $D\Gamma B^{\delta-1}$, and the agreement between these quantities constitutes a nontrivial test of the validity of the equation of state.

E. "Modified MLSG" equation

As we shall see below, the MLSG equation does not fit specific-heat data on all available systems, and it is useful to search for alternate forms. Since we must resort to numerical techniques to calculate the specific heat with the MLSG equation, it is relatively simple to generalize the model, in order to gain additional flexibility in fitting the experimentally determined critical ratios. We have investigated the following "modified MLSG" equation, which required only minimal changes in the existing computer programs, but contained an additional parameter, e_3:

$$\tilde{h}(\tilde{x}) \equiv (1+e_2)^{-(\gamma-1)/2\beta e_3}(1+\tilde{x}) \times[1+e_2(1+\tilde{x})^{2\beta e_3}]^{(\gamma-1)/2\beta e_3}. \quad (3.15)$$

[The parameter e_2 plays the same role as E_2 in Eq. (3.14), but we have changed the notation since e_2 will differ from E_2 for $e_3 \neq 1$.] As a result of the introduction of e_3, the analytic behavior of $\tilde{h}(\tilde{x})$ for large $\tilde{x}$ is modified, and becomes

$$\tilde{h}(\tilde{x}) \underset{\tilde{x}\to\infty}{\sim} \tilde{\eta}_1\tilde{x}^{\gamma}+\tilde{\eta}_2\tilde{x}^{\gamma-2\beta e_3}+\tilde{\eta}_3\tilde{x}^{\gamma-1}+\cdots, \quad (3.16)$$

whereas the correct behavior is [see Eq. (C4)]

$$\tilde{h}(\tilde{x})=\sum_{n=0}^{\infty}\tilde{\eta}_{n+1}\tilde{x}^{\gamma-2\beta n}. \quad (3.17)$$

Thus, although the leading power of $\tilde{x}$ is independent of e_3, the second term in Eq. (3.16) is incorrect for $e_3 \neq 1$, whereas in the MLSG equation ($e_3=1$) only the third and following terms are wrong. It is clear, however, that this error primarily affects the analytic properties of higher derivatives of the free energy, which are less accessible to experiment than the specific heat. The effect of e_3 on A/A' is illustrated in Fig. 6, from which the additional flexibility in fitting experimental data is apparent, since e_2 may still be varied. It must be noted, however, that not all pairs of values of e_2 and e_3 will lead to sensible results; for instance, for some values of e_3 the coefficients A or A' turn out to be negative. We have not made a systematic study of the allowable range of parameters, since we do not ascribe any particular theoretical significance to this modified MLSG equation. In practice, one can attempt to determine e_2 and e_3 by fitting to A/A' and Γ/Γ' (with fixed exponents), and then see whether the ratio $D\Gamma B^{\delta-1}$ agrees with experiment.

For illustrative purposes we show, in Fig. 7, the functions $\tilde{h}(\tilde{x})$ and $\tilde{h}''(\tilde{x})$, for the MLSG and modified MLSG equations (MMLSG), which have the same critical exponents and the same value of

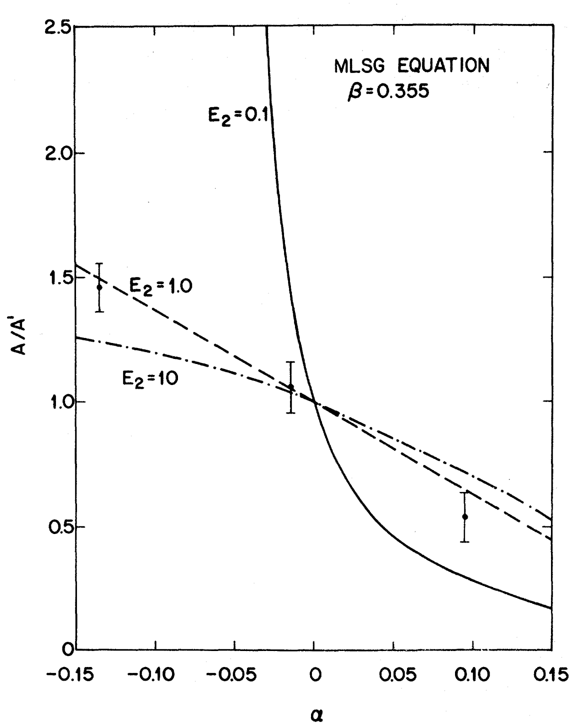

FIG. 5. Amplitude ratio A/A' as a function of α for the MLSG equation with $\beta=0.355$. The experimental A/A' ratios are the same as in Fig. 2. A value of the parameter E_2 may be found to fit the experimental A/A' in each of these systems.

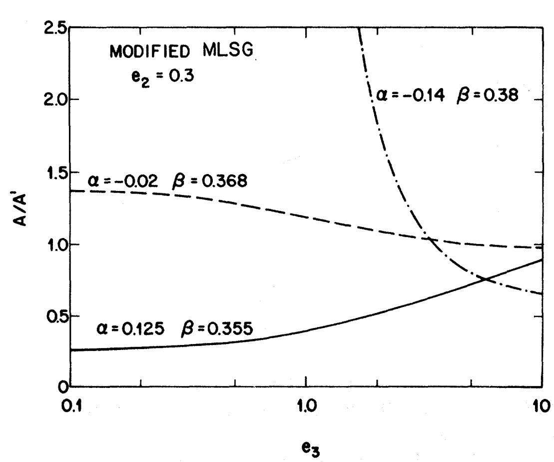

FIG. 6. Amplitude ratio A/A' as a function of the parameter e_3 in the modified MLSG equation, for typical values of the exponents, and a fixed value of e_2. $e_3=1$ corresponds to the MLSG equation, with $E_2=e_2$.

Γ/Γ'. It is seen that the function $\tilde{h}(\tilde{x})$ is almost indistinguishable for the two cases, whereas $\tilde{h}''(\tilde{x})$ differs, and leads to the amplitude ratios $(A/A')_{\rm MLSG} = 0.52$ and $(A/A')_{\rm MMLSG} = 0.54$ in this case.

F. Field-dependent specific heat

Having fixed the parameters of the equation of state, the singular part of the specific heat is fully determined in the (ρ, T) or (M, T) plane. The relevant equations are given in Appendixes C, D, and E. Note that to go from the expression in universal variables, $\tilde{C}(t, \tilde{H})$, to one in the usual dimensionless units, $C(t, H)$, the field $\tilde{H}$ must be multiplied by the scale factor $H_0 = H/\tilde{H} = x_0^{-\beta\delta} h_0$, and the specific heat must be multiplied by $C_0 = C/\tilde{C} = h_0 x_0^{\alpha-2}$. Once the scale factors x_0 and h_0 have been determined from the measured values of B and Γ via Eqs. (2.9) and (2.10), the specific heat can be expressed in dimensionless or dimensioned units, and compared with experiment. In zero field, once the universal parameters α and A/A' agree with experiment, there is only one relevant parameter left to fit, say the amplitude $A - A'$. In finite field the full equation of state may be tested. For example, the specific heat along the critical isotherm behaves as

$$C(t=0, H) = A_H H^{-\alpha/\beta\delta}, \tag{3.18}$$

and both the exponent and the amplitude can be compared with experiment.

As an illustration of the effect of fields on the specific heat, we have plotted the difference $\tilde{C}_H(\tilde{H}, t) - \tilde{C}_H(0, t)$ vs t for various values of $\tilde{H}$ in Fig. 8, using the modified MLSG equation with parameters appropriate to Ni (see Sec. IV). Since we have expressed the results in universal units, we expect them to apply semiquantitatively to other ferromagnets, if the appropriate scale factors H_0, H_N, C_0, and C_N are used [see Eqs. (B2), (B4), (B9), and (B10)]. A general feature which is apparent from Fig. 8 is that for each value of the field there is a characteristic temperature $t_0(\tilde{H})$ at which the field effects become appreciable, and from the scaling properties we may write

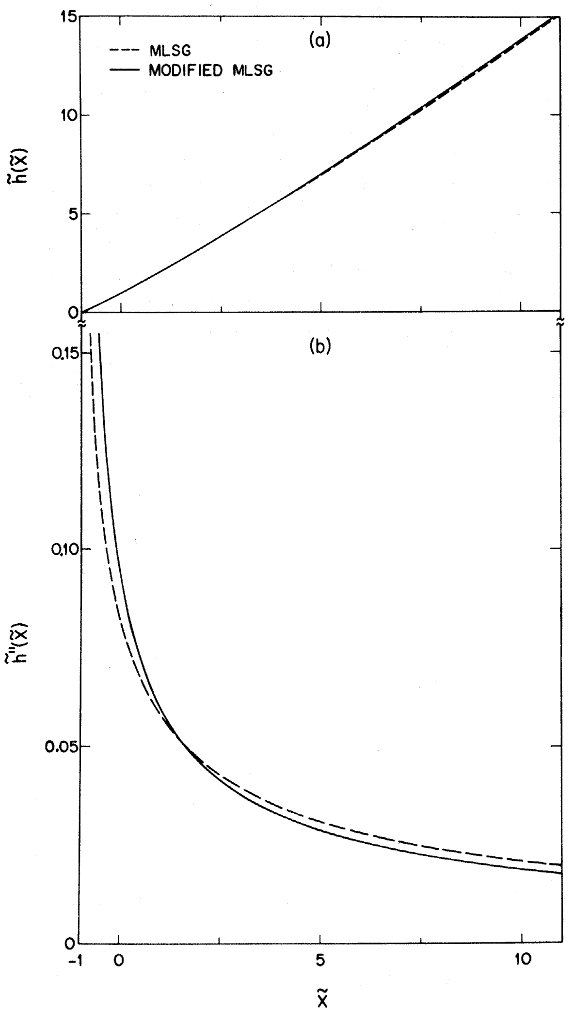

FIG. 7. Comparison of MLSG equation and modified MLSG equation. The exponents and critical ratio Γ/Γ' have been fixed to the values $\alpha = 0.095$, $\beta = 0.3475$, $\Gamma/\Gamma' = 4.05$ for both equations. The universal parameters are $E_2 = 0.2534$ (MLSG) and $e_2 = 0.4605$, $e_3 = 0.6869$ (modified MLSG). Note that $\tilde{h}(\tilde{x})$ is almost identical in both cases, but deviations appear in the second derivative $\tilde{h}''(\tilde{x})$.

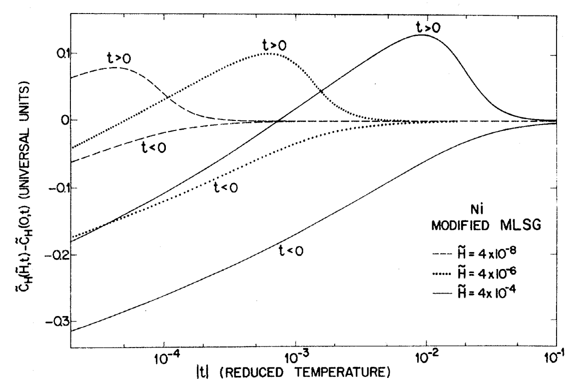

FIG. 8. Specific-heat difference $\tilde{C}_H(\tilde{H}, t) - \tilde{C}_H(0, t)$ vs reduced temperature for various values of the reduced field $\tilde{H}$ according to the modified MLSG equation. The parameters chosen are appropriate to Ni ($\alpha = -0.091$, $\beta = 0.378$, $e_2 = 2.361$, $e_3 = 0.541$), but similar curves are expected for other materials since universal units are used. For $t > 0$, $\tilde{C}_H(\tilde{H}, t) - \tilde{C}_H(0, t)$ has a positive maximum at a reduced temperature which increases with increasing $\tilde{H}$. For $t < 0$, the specific-heat difference is always negative.

$$t_0(\tilde{H}) = \tilde{H}^{1/\beta\delta}. \tag{3.19}$$

For the example treated in Fig. 8, we have, for instance, $t_0 = 7\times10^{-4}$ for $\tilde{H} = 4\times10^{-6}$ (corresponding to $H = 90$ Oe), which locates the maximum of the dotted curve. The temperature $t_1(\tilde{H})$ at which field effects first appear is roughly one order of magnitude higher, i.e., $t_1 \approx 10t_0$.

IV. FITS TO SPECIFIC SYSTEMS

In this section we report the results of our attempts to fit various equations of state to specific-heat data on a number of systems. The equations we use are determined from *PVT* or *MHT* data, but these data sometimes allow a rather large variation in the parameters. From the discussion of Sec. III, it should be clear that the additional requirement that the specific heat should also fit narrows down the set of permissible equations, and serves to define the parameters of the "successful" equations to a considerable degree. It should be stated at the outset that the concrete results of our work are not to be taken as a claim for a correct equation of state, consistent with specific-heat data. We have not undertaken any careful study of the correlations between the errors in determining various parameters, such as was carried out in Refs. 4 and 5, for *PVT* data on fluids. On the other hand, some of the inconsistencies we point to are of a gross nature, and they may thus be demonstrated by a relatively crude analysis. A disagreement between *PVT* and specific-heat fits to the linear model in ^{3}He had been noted earlier by Huang and Ho.[5]

A. Ising and Heisenberg models

The equation of state for the three-dimensional Ising model was obtained from a series analysis by Gaunt and Domb.[15] The results were fitted to both the MLSG equation and the linear model (LM), with parameters

$$E_2 = 0.3242 \tag{4.1}$$

and

$$b^2 = 1.5, \tag{4.2}$$

respectively, and with exponents $\alpha = 0.125$ and $\beta = 0.3125$. The ensuing values for the critical ratios are as follows:

MLSG:

$$A/A' = 0.51, \quad \mathcal{P} = 3.90, \quad \Gamma/\Gamma' = 5.02, \quad D\Gamma B^{\delta-1} = 1.756; \tag{4.3}$$

LM:

$$A/A' = 0.50, \quad \mathcal{P} = 4.03, \quad \Gamma/\Gamma' = 5.44, \quad D\Gamma B^{\delta-1} = 1.78. \tag{4.4}$$

The last two ratios are to be compared with the direct series estimates[15]

$$\Gamma/\Gamma' = 5.07, \quad D\Gamma B^{\delta-1} = 1.756. \tag{4.5}$$

Alternatively, we may determine the parameters e_2 and e_3 for the modified MLSG equation by fitting to the values of Γ/Γ' and $D\Gamma B^{\delta-1}$ in (4.5), which yields

$$e_2 = 0.3045, \quad e_3 = 1.0336, \tag{4.6}$$

and also

$$A/A' = 0.506. \tag{4.7}$$

Using the scale variables[15] $x_0 = 0.270$, $e_1 = E_1 = 0.308$, valid for the bcc lattice, we then find

$$A = 0.138. \tag{4.8}$$

These results may be contrasted with the direct series estimated for a tetrahedral lattice,[30]

$$A/A' = 0.75, \tag{4.9}$$

$$A = 0.15. \tag{4.10}$$

Comparing (4.10) with (4.8) we conclude that the high-temperature series for the specific heat are rather reliable, since A is not expected to vary significantly between different three-dimensional lattices. On the other hand, we interpret the discrepancy between the A/A' values in (4.9) and (4.7) as evidence against the low-temperature series. Moreover, the finite value of Q [Eq. (3.10)] obtained in the series analysis (see Table I) is consistent with the equation of state derived in Ref. 15, which has no singular correction terms.

The preceding discussion illustrates the usefulness of empirical fits to the equation of state, if these have a simple closed form and possess enough free parameters to represent the data adequately. In particular, we conclude that for the Ising model the MLSG equation already represents the series results to within their probable errors, and the modified MLSG equation is not necessary. With either equation, it is very simple to obtain A and A', and thus to test the specific-heat series. Similarly, it might be useful to fit the results of the ϵ expansion[16] to a closed-form expression. An analysis of the Ising equation of state in terms of improved parametric representations has recently been carried out by Tarko and Fisher,[19] but no estimates were made of the specific heat.

A recent fit of the Ising equation of Ref. 15 by Krasnow and Stanley[32] leads to a ratio $A/A' = 3.15$, which disagrees significantly with our answer, and is clearly incorrect. In fact, Krasnow and Stanley calculate the specific heat C_M, which in general differs from C_H on the coexistence curve. The authors assert[33] that this difference vanishes because $\tilde{h}(\tilde{x}) \sim (\tilde{x}+1)^q$ for $\tilde{x} \to -1$, with $q > 1$, which is correct in the Heisenberg model [cf. Eq. (2.11)], but incorrect in the Ising case. Their value of $q = 1.076$ (Table I of Ref. 32) should be replaced by $q = 1$, which is almost certainly also consistent with the data. Then C_M differs from C_H, and the value quoted in their Table II refers to C_M, while C_H leads to the ratio given in Eq. (4.7) above.

In the Heisenberg case $C_M = C_H$ on the coexistence curve, and the ratio found by Krasnow and Stanley for $S = \infty$, $A/A' = 1.46$, is in remarkably good agreement with the experimental value for $RbMnF_3$ given in Table II, $A/A' = 1.46$. The ratio A/A' should be independent of spin, and we consider the $S = \frac{1}{2}$ value in Ref. 32, $A/A' = 2.64$, to be less reliable.

B. Xenon and CO_2

Thermodynamic *PVT* data on Xe and CO_2 have been analyzed with great care by Levelt Sengers *et al.*[4] and fitted to both the MLSG and linear-model equations of state. For CO_2 White and Maccabee[34] have also carried out a linear-model analysis. With the parameters thus determined, we may calculate the specific heat according to the formulas of Appendices C, D, and E. The results are shown in Tables III and IV for the linear model and MLSG equations of state, respectively. The specific-heat data of Ref. 35 for Xe and Ref. 36 for CO_2 are shown in Figs. 9 and 10, along with the predictions of the linear-model and MLSG equations, using parameters obtained from Tables III and IV. In comparing theory and experiment we have used Eqs. (3.9c) and (3.9d), and have adjusted the values of B_0 and T_c, with A, A', and α fixed at their MLSG values, to obtain the best fit. It is seen that the fit for Xe is satisfactory, but the deviations in CO_2 are probably outside the experimental errors. Similar plots for the other parameter sets appropriate to Xe and CO_2 given in Tables III and IV yield comparable, though in general poorer results, which we attribute to errors in the values of α and A/A' obtained from the linear-model and MLSG equations.

The fits to the specific-heat data obtained in Refs. 35 and 36 possess a jump Q [Eq. (3.10)] which is inconsistent with the equations of state we are considering. We have therefore reanalyzed the data in order to obtain a fit with a pure power law and a smooth background [Eqs. (3.9c) and (3.9d)]. For Xe and CO_2, the data used in the fit covered essentially the same temperature range as the previous analyses.[35,36] The results are given in Table V, and show a rather large change in A/A' for Xe. It must also be stated that imposition of the constraint $Q = 0$ ($B_0 = B_0'$) considerably worsens the fit to the data for CO_2, and we do not understand this behavior. In particular we do not know whether it is associated with a systematic experimental error or whether, on the contrary, it is an intrinsic property which requires theoretical interpretation. In any case, the α and A/A' values we quote for CO_2 should be treated with caution, since they result from imposing the constraint $B_0 = B_0'$, which is not statistically allowed by the data.

Despite these uncertainties, we shall illustrate the use of the modified MLSG equation by attempting to find parameters for this equation which fit both the *PVT* data and the specific heat. The procedure we adopt is the following: The parameters β, B, α, and A/A' are fixed at their experimental values, determined by least-squares fits to experimental data (see Table V). The ensuing value of γ, determined by scaling, is not the best-fit value, so that we cannot use the experimental

TABLE III. Universal and scaling parameters from analyses of the linear model.

System	α	β	a	k	b^2	A/A'	Γ/Γ'	$D\Gamma B^{\delta-1}$	A (J mole^{-1} K^{-1})	ΔC [c] (J mole^{-1} K^{-1})	Reference
CO_2	0.104	0.3486	28.02	1.828	1.80	0.427	4.60	1.60	5.017	132.9	4
CO_2	0.104	0.3486	21.84	1.413	1.382 [b]	0.476	4.16	1.53	6.086	131.9	4
CO_2	0.106	0.347	23.0	1.3	1.3	0.469	4.23	1.54	6.901	153.1	34
Xe	0.089	0.350	17.68	1.315	1.407	0.536	4.18	1.55	5.068	91.19	4
Ni	−0.109	0.378	0.92	1.36	1.809	2.048	3.86	1.72	1.375	13.7	38
EuO	−0.0093	0.368	2.689 [a]	1.08	1.598	1.067	3.98	1.62	2.630	18.83	22
EuO	−0.0598	0.385	2.327 [a]	1.27	2.00	1.575	3.70	1.60	2.071	19.13	23

[a] See footnote 37.

[b] "Restricted" linear-model value.

[c] $\Delta C \equiv C(t = -10^{-3}) - C(t = 10^{-3})$.

TABLE IV. Universal and scaling parameters for the MLSG equation from the analysis of Levelt Sengers *et al.* (Ref. 4).

System	α	β	x_0	E_1	E_2	A/A'	Γ/Γ'	$D\Gamma B^{\delta-1}$	A (J mole^{-1} K^{-1})	ΔC[a] (J mole^{-1} K^{-1})
CO_2	0.104	0.3486	0.1419	2.178	0.2534	0.445	4.24	1.58	5.605	137.8
Xe	0.065	0.350	0.186	2.728	0.3507	0.651	4.06	1.57	6.879	88.85

[a] $\Delta C \equiv C(t=-10^{-3}) - C(t=10^{-3})$.

value of the amplitude Γ. Instead, we choose the Γ which best fits the compressibility data with γ held fixed. Having determined the exponents and the scales [see Table V] one might wish to determine e_2 and e_3 [Eq. (3.14)] by fitting to Γ/Γ' and $D\Gamma B^{\delta-1}$, and then test the quality of the fit to A and A'. In practice, however, the errors in the experimental knowledge of Γ/Γ' and $D\Gamma B^{\delta-1}$ are rather large, and we have chosen to determine e_2 and e_3 by fitting to A and A' (or A/A' and $A-A'$) calculated using the formulas of Appendix D. The resulting values of Γ/Γ' and $D\Gamma B^{\delta-1}$, shown in Table VI, are consistent with the experimental values, within rather large uncertainties. With the introduction of the additional parameter e_3, we have thus been able to obtain a perfect fit to the specific heat in the reduced-temperature interval $|t_{min}| < |t| < |t_{max}|$ (see the solid line in Figs. 9 and 10), using an equation of state which is consistent with *PVT* data, at least at the presently available level of accuracy.

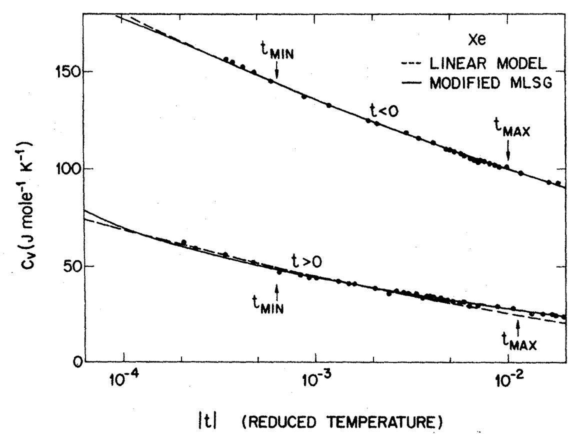

FIG. 9. Comparison of the linear model and modified MLSG fits to the Xe specific-heat measurements of Edwards *et al.* (Ref. 35). The linear-model parameters α, A/A', and A are those of Levelt Sengers *et al.* (Ref. 4 and Table III). Holding these parameters fixed, a least-squares fit of the data to Eqs. (3.9c) and (3.9d), for $|t_{min}|<|t|<|t_{max}|$, yielded the values $T_c = 289.72$ K and $B_0 = -59.83$. The reduced temperatures in the figure are relative to this value of T_c. The solid line represents the result of the modified MLSG equation, whose parameters were determined by fitting to these data in the interval $|t_{min}|<|t|<|t_{max}|$.

Returning to the MLSG equation, we note that for Xe, the exponent α predicted[4] from scaling has the low value 0.065, and this is certainly not the best value. The fact that the "best exponents" determined from different sets of data may not satisfy scaling, presents a fundamental difficulty, which cannot be cured by the introduction of an additional universal parameter in the equation of state. Rather, it seems to be an indication that singular correction terms are needed. The analogous situation occurred in our analysis, described above, where β and α were fixed from the data, and γ then was found to deviate somewhat from its best value.[4] The introduction of singular correction terms is a rather complicated procedure, since these involve a new scaling function[8] and new unknown exponents,[9] so that in order to carry out the analysis in practice, a great deal of theoretical input will be necessary.

In concluding this section we may say that more

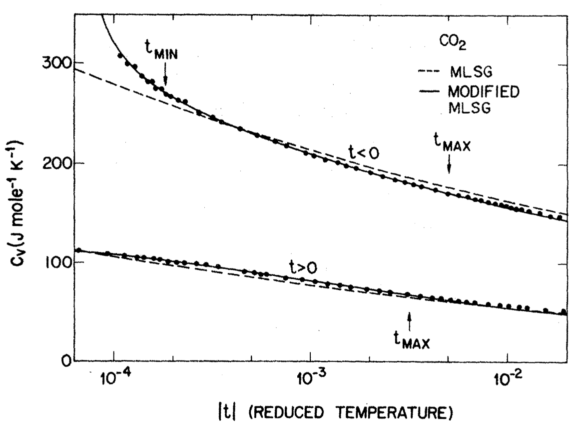

FIG. 10. Comparison of the MLSG and modified MLSG fits to the CO_2 specific-heat data of Lipa *et al.* (Ref. 36). As in Fig. 9, the data were fitted to the MLSG equation with A/A', α, and A fixed from Ref. 4 (see Table IV), to obtain $T_c = 303.95$ K and $B_0 = -33.97$. The modified MLSG equation (solid line) is adjusted to fit the data in the interval $|t_{min}|<|t|<|t_{max}|$. Note that the data are plotted relative to the T_c obtained above from the MLSG analysis.

TABLE V. Reanalysis of specific-heat measurements and parameters used in the modified MLSG equation.

System	α	A/A'	A (J mole^{-1} K^{-1})	B_0 (J mole^{-1} K^{-1})	E_0 [p] (J mole^{-1} K^{-1})	ΔC [q] (J mole^{-1} K^{-1})	T_c (K)	Range t_{min}	Range t_{max}	β	B	γ	Γ
CO_2	0.0949 [a]	0.538 [a]	7.226 [a]	−64.72 [a]		126.17 [a]	303.924	$\pm 1.0\times 10^{-4}$	$\pm 5.0\times 10^{-3}$	0.3475 [b]	1.957 [b]	1.21 [c]	0.061 [d]
Xe	0.1105 [e]	0.440 [e]	3.755 [e]	−0.287 [e]		92.94 [e]	289.728	$+6\ \times 10^{-4}$ $-8\ \times 10^{-4}$	$\pm 1.0\times 10^{-2}$	0.355 [f]	1.18 [c]	1.18 [c]	0.012 [g]
Ni	−0.0908 [h]	1.40 [h]	1.933 [h]	47.02 [h]	14.83 [h]	3.19 [h]	631.415	$+1.3\times 10^{-3}$ -7.0×10^{-4}	$\pm 1.0\times 10^{-1}$	0.378 [i]	1.422 [i]	1.33 [c]	1.346 [j]
EuO	−0.0445 [k]	1.22 [k]	3.941 [k]	103.75 [k]	27.54 [k]	11.83 [k]	69.372	$+4.0\times 10^{-3}$ -6.0×10^{-3}	$\pm 7.0\times 10^{-2}$	0.368 [m]	1.255 [m]	1.31 [c]	0.370 [n]

[a] Reanalysis of specific-heat data of Lipa *et al*. (Ref. 36).
[b] J. M. H. Levelt Sengers, J. Straub, and M. Vicentini-Missoni, J. Chem. Phys. 54, 5034 (1971).
[c] Obtained from scaling.
[d] Least-squares fit to data from J. H. Lunacek and D. S. Cannell, Phys. Rev. Lett. 27, 841 (1971), using scaled γ.
[e] Reanalysis of specific-heat data of Edwards *et al*. (Ref. 35).
[f] J. M. H. Levelt Sengers, Physica 73, 73 (1974); and R. Hocken (private communication).
[g] Least-squares fit to data in footnote f using scaled γ.
[h] Data of Ref. 39, reanalyzed in Ref. 31.
[i] J. S. Kouvel and J. B. Comly, Phys. Rev. Lett. 20, 1237 (1968).
[j] Least-squares fit to data in footnote i using scaled γ.
[k] A. Kornblit and G. Ahlers (Ref. 40).
[m] N. Menyuk, K. Dwight, and T. B. Reed, Phys. Rev. B 3, 1689 (1971).
[n] Least-squares fit to data in footnote m using scaled γ.
[p] For EuO and Ni the term $C_B(t)$ [Eqs. (A4) and (A5)] is written as $C_B(t) = B_0 + E_0 t$.
[q] $\Delta C \equiv C(t=-10^3) - C(t=10^{-3})$.

TABLE VI. Universal and scaling parameters for the modified MLSG equation. (The experimental numbers are obtained from Table V.)

System	α	β	x_0	e_1	e_2	e_3	A/A'	Γ/Γ'	$D\Gamma B^{\delta-1}$	A (J mole^{-1} K^{-1})	ΔC [a] (J mole^{-1} K^{-1})
CO_2	0.0949	0.3475	0.1448	2.173	0.3458	1.0120	0.538	3.95	1.50	7.226	126.17
Xe	0.1105	0.355	0.2067	1.963	0.550	0.3654	0.440	4.26	2.05	3.755	92.77
Ni	−0.0908	0.378	0.3940	0.1023	2.361	0.5142	1.40	1.26	1.36	1.933	11.30
EuO	−0.0445	0.368	0.5813	1.294	1.046	0.7160	1.22	2.65	1.48	3.941	21.98

[a] $\Delta C \equiv C(t=-10^{-3}) - C(t=10^{-3})$.

accurate experimental data on the critical exponents and amplitudes of fluids are needed before the details of the equation of state are clarified.

C. Ferromagnets EuO and Ni

Data on the equation of state of magnetic systems have not been analyzed with as much care as for fluids, but a number of specific equations have been proposed in the literature.[2,22-24] We have chosen to study EuO and Ni since both specific-heat and MHT data are available on these systems. One important motivation for our work is the desire to estimate the effect of small magnetic fields (e.g., the earth's field) on the specific-heat singularity. For this purpose it is important to have a numerically accurate equation of state rather than one which satisfies all the known analyticity requirements.

The linear-model parameters have previously been determined[37] for[22,23] EuO and [38] Ni and it is straightforward to calculate A/A' and $A-A'$ from Eqs. (E18) and (E19). The results for EuO and Ni, shown in Table III, are quite different from the best values of A and A', and the ensuing specific heat will disagree strongly with the experimental data (see below). This comparison demonstrates quite clearly the inapplicability of the linear model for representing the specific heat. In fact, as shown in Sec. III, there is no way to obtain the experimental A/A' of Ni (~ 1.4) shown in Table II, in the linear model with realistic exponent values. The MLSG equation can be made to fit A/A', with a proper choice of E_2 (see Fig. 5), but there remains a large discrepancy in the absolute value of $A-A'$, which shows that an inconsistency remains.

We have therefore undertaken to fit the data with the modified MLSG equation. The input parameters for our analysis were β, B, α, and A/A' taken from experiment. The amplitude Γ was again found by a fit with γ fixed at its value determined by scaling. The ensuing parameters, shown in Table V, determine the scale parameters x_0 and $E_1 = e_1$. The universal parameters e_2 and e_3 could then be found by fitting to A/A' and $D\Gamma B^{\delta-1}$ (as mentioned earlier Γ/Γ' is probably rather difficult to interpret in these systems). Since the uncertainties in $D\Gamma B^{\delta-1}$ are rather large, we have instead obtained e_2 and e_3 by fitting to the experimental A/A' and $A-A'$, thus obtaining the specific heat exactly, within the temperature range of the fit. The ensuing values of $D\Gamma B^{\delta-1}$ and Γ/Γ' (Table VI) are rather different from those obtained from the linear model in Table III but agree more closely with series estimates for the Heisenberg model[32] ($D\Gamma B^{\delta-1} = 1.23$ for $S=\infty$, $D\Gamma B^{\delta-1} = 1.54$ for $S=\frac{1}{2}$, $\Gamma/\Gamma' = 0$ for both cases). Direct experimental determinations of $D\Gamma B^{\delta-1}$ and Γ/Γ' are not available at present, but would of course be desirable.

We have summarized the numerical data on scales and normalizations for CO_2, Xe, Ni, and EuO in Table VII. An interesting conclusion which may be drawn from this table is that the scale

TABLE VII. Normalizations and scales.

System	C_0 [a]	C_N (J mole^{-1} K^{-1})	H_0 [a]	H_N (Oe)	M_0 [a]	M_N (emu mole^{-1})	ρ_0 [a]	ρ_N (g cm^{-3})	μ_0 [a]	μ_N (cm^2 sec^{-2})
CO_2	94.27	2.29 [b]					1.96	0.466 [b]	48.17	1.58×10^{8} [b]
Xe	52.27	2.40 [b]					1.75	1.11 [b]	29.87	5.25×10^{7} [b]
Ni	2.0513	R [c]	1.443	1.52×10^{7} [d]	1.42	3.44×10^{3} [d]				
EuO	5.965	R [c]	4.886	1.52×10^{5} [e]	1.22	3.80×10^{4} [e]				

[a] Parameters obtained from Table VI.
[b] Reference 14.
[c] Gas constant $R = 8.3167$ J mole^{-1} K^{-1}.
[d] Reference 24.
[e] Reference 23.

of fields $H_N H_0$ [see Eqs. (B2) and (B9)] is an order of magnitude larger for Ni than for EuO. Thus, since the universal parameters are comparable in the two substances, a given magnetic field (e.g., the earth's field) will have roughly 10 times more effect in EuO than in Ni.

In Fig. 11, we show the prediction of the linear model[38] for the specific heat of Ni, and compare it to the measurements of Connelly *et al.*[39] As in the case of the fluids, the values of B_0 and T_c were determined from a least-squares fit to Eqs. (3.9c) and (3.9d) using the Ho parameters[38] (see Table III). The data and curves are plotted relative to Ho's adjusted T_c, which is far below the modified MLSG transition temperature, determined by fitting to the specific-heat data. (This leads to the unusual shape of the experimental and modified MLSG curves for $t>0$.) It is clear from Fig. 11 that the linear-model fit is in very poor agreement with experiment, especially for $t>0$. This disagreement is to be expected since the linear model does not provide the correct experimental A/A'.

Having determined a set of parameters to fit both the *MHT* data and a zero-field specific heat for EuO,[22,23,40] and Ni,[24,39] we may calculate the field-dependent specific heat. We find that even a small magnetic field leads to a significant rounding in the specific heat near the transition,

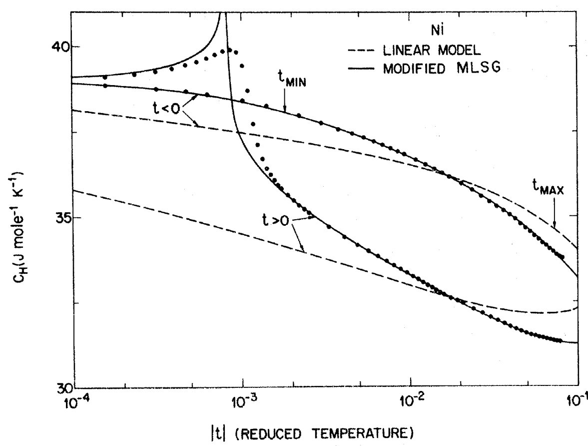

FIG. 11. Comparison of the linear-model prediction for the specific heat C_H of Ni with the measurements of Connelly *et al*. (Ref. 39) in zero applied field. The linear-model parameters of Ho (Ref. 38) were used to determine α, A/A', and A (see Table III). A least-squares fit of the data to Eqs. (3.9c) and (3.9d) with α, A, and A' fixed, gave $T_c=630.90$ K, $B_0=40.39$. The solid curve is the prediction of the modified MLSG equation, whose parameters were obtained by fitting to the data in the range $|t_{\min}|<|t|<|t_{\max}|$. The reduced temperatures are relative to the linear-model T_c, which differs from the T_c used in the modified MLSG analysis.

as can be seen for Ni in Fig. 12. The modified MLSG equation has been adjusted to fit the specific heat at "zero field" in the temperature region $|t|\gtrsim 10^{-3}$, and the extrapolated zero-field behavior in the rounded region ($|t|<10^{-3}$) is shown by the dashed curve in Fig. 12. An effective field of only $H=2.5$ Oe is sufficient to reduce the specific-heat maximum to its experimental value, and to approximate the shape of the curve reasonably well in the inner region. It is also interesting to note that a significant fraction of the measured specific-heat increase due to the phase transition is situated in the rounded region, at least above T_c.

The calculated field-dependent specific heat in larger magnetic fields is presented in Fig. 13 for Ni, along with experimental data from Ref. 39. As mentioned above, there is a rather significant deviation between the zero-field curves for T close to T_c. At finite field, the agreement is only semiquantitative even for $|t|>10^{-3}$, and it appears to improve with increasing field. A more careful comparison between experiment and theory is needed before a definitive conclusion can be drawn. In particular, the field H which enters the equation of state is only equal to the applied field H_a when demagnetizing effects can be neglected. There is some indication that this is a reasonable assumption in the experiments of Ref. 39, since the field dependence of C_H is correctly predicted by our theory for $T<T_c$ (e.g., $T=630$ K), taking H to be the applied field. (Demagnetizing

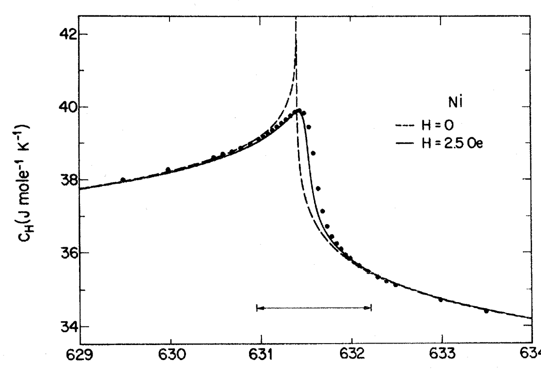

FIG. 12. Specific heat of Ni as a function of temperature near the Curie point. The data are those of Connelly *et al*. (Ref. 39). The temperature region shown by the arrows was excluded from the zero-field analysis (see Table V). The dashed curve is the ideal zero-field behavior obtained from the modified MLSG equation. An effective internal field of $H=2.5$ Oe and a shift of 0.02 K in T_c (solid line) yield a reasonable fit to the specific-heat measurements near T_c.

effects should become important when the magnetization is appreciable, i.e., for low temperatures.) A careful discussion of the influence of demagnetizing effects on the specific heat has been given by Griffiths,[41] and his theory could be combined with our equation of state to calculate the specific heat as a function of H_a for well-defined sample shapes.

The data in Fig. 13 had previously been compared to theoretical equations of state,[38,32] but only in scaled form, i.e., $[C_H(H,t) - C_H(0,t)]H^{\alpha/\beta\delta}$ vs $tH^{-1/\beta\delta}$. We have reproduced such a comparison in Fig. 14, except that we have used universal units; i.e., we have plotted $[\tilde{C}_H(\tilde{H},t) - \tilde{C}_H(0,t)]\tilde{H}^{\alpha/\beta\delta}$ vs $t\tilde{H}^{-1/\beta\delta}$. It is seen that a scaled plot is rather insensitive, since the linear model apparently fits the data quite well, even though the zero-field prediction is very inaccurate (Fig. 11). In fact the linear-model prediction for the difference $C_H(t,H) - C_H(t,0)$ agrees reasonably well with the modified MLSG calculation shown in Fig. 8.

Since Fig. 14 is in universal units it should apply roughly to EuO also. However, data do not exist with finite applied field, so we only show in Fig. 15 our zero-field result from the modified MLSG equation, along with the data of Ref. 40. In an attempt to understand the rounding of the data near T_c, we have also calculated the specific heat in the presence of the earth's field ($H = 0.3$ Oe). The results shown in Fig. 15 display a non-negligible field effect at $|t| < 10^{-3}$. However, it is quite evident from the shape of the data very near T_c that other contributions, such as inhomogeneities or imperfections, must also play a role

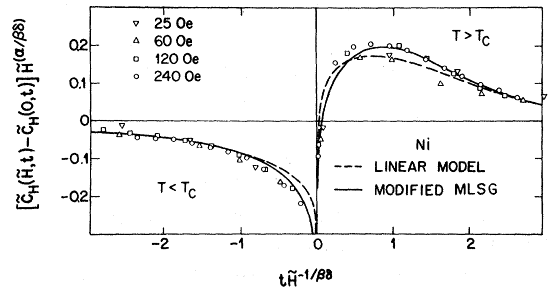

FIG. 14. Scaled specific heat in finite magnetic field, using universal units. The data are the same as in Fig. 13. The dashed and solid curves correspond to the predictions of the linear model (Ho parameters, Ref. 38) and modified MLSG equations of state, respectively. (See Tables III and V.)

in the specific-heat rounding, for the sample used in Ref. 40.

D. Antiferromagnets and liquid helium

In the case of antiferromagnets or of the ^{4}He λ transition, the field conjugate to the order parameter is not physically accessible, so that experimental data are confined to the critical isochore and coexistence curve. In order to find an approximate equation of state, we have used the MLSG equation, with γ obtained from theory,[20,28] and α and A/A' from experiment.[11,42] This information is sufficient to determine the equation of state in universal units, since there is only one free parameter, E_2, which is fitted to A/A'. The results for $RbMnF_3$, FeF_2, and

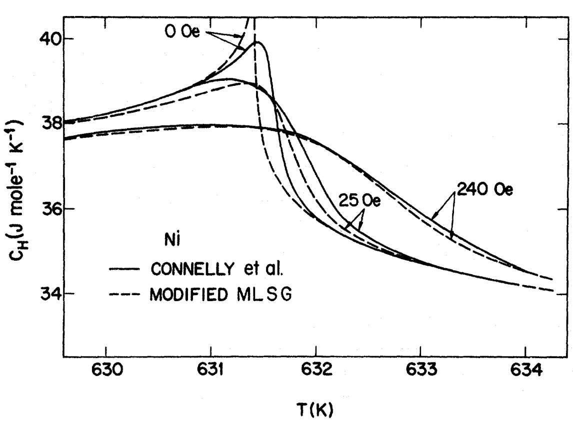

FIG. 13. Specific heat of Ni in a magnetic field as a function of temperature. The solid curves correspond to the measurements of Connelly *et al.* (Ref. 39). The dashed curves are the predictions of the modified MLSG equation. Agreement between theory and experiment improves as the field is increased. Note that demagnetization corrections have been neglected in this comparison.

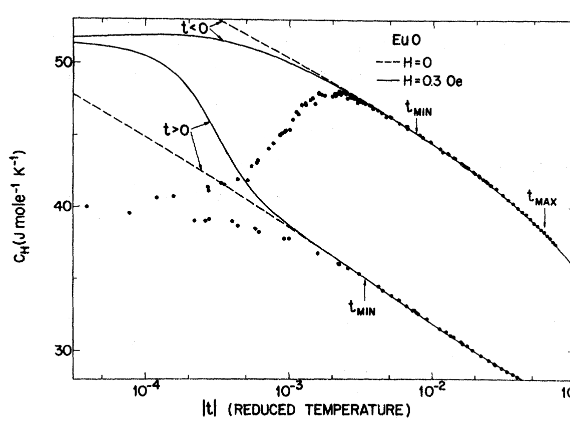

FIG. 15. Specific heat of EuO vs reduced temperature. The data are those of Kornblit and Ahlers (Ref. 40). The solid curve represents the expected specific heat in the earth's magnetic field ($H \simeq 0.3$ Oe) using the modified MLSG equation and neglecting demagnetizing effects. The dashed curve is the zero-field prediction. The modified MLSG analysis was carried out for data in the temperature range between $|t_{min}|$ and $|t_{max}|$.

^{4}He are presented in Table VIII. With the linear model, no value of b^2 can be found to fit the experimental A/A', unless the exponents are drastically changed (see Sec. III).

V. CONCLUSIONS

Let us conclude by summarizing the principal results of the present work.

(i) A general scheme is discussed for determining the equation of state of a substance near the critical point, by fitting to experimental data. The distinction between "universal" and "nonuniversal" parameters is emphasized, and the utility of fitting amplitude ratios to determine universal parameters is pointed out. Special emphasis is placed on the specific heat along the critical isochore (or in zero field). For this quantity a body of reliable data exists, which may be understood reasonably well in terms of universality classes.

(ii) The amplitude ratio A/A' for the specific-heat singularity above and below T_c is calculated using previously proposed scaled equations of state. The MLSG equation can be made to fit experimental and theoretical values of A/A' for both Ising-like and Heisenberg-like systems, by adjusting a single parameter E_2, using reasonable exponent values. The ensuing values of other amplitude ratios are then in rough agreement with experiment. Using the linear-model equation of state, similar agreement can be found for Ising-like systems, but only for a very restricted range of exponent values, which may not yield the "best fit" to experimental data. For Heisenberg-like systems, the linear model cannot be made consistent with the expected range of A/A' values ($1.2 \sim 1.6$), without choosing unrealistic values for the exponents ($\beta \lesssim 0.3$).

(iii) Specific-heat data on Xe and CO_2 are analyzed, and compared to the predictions of the MLSG and linear-model equations, with parameters determined by Levelt Sengers *et al.*,[4] and White and Maccabee.[34] The linear-model analysis of Levelt Sengers *et al.*[4] gives the best fit for Xe, but still shows a small discrepancy ($\simeq 5\%$) for $t>0$. In CO_2, there is a slightly larger discrepancy ($\gtrsim 10\%$) between the data and the predictions of both the linear-model and MLSG equations.

(iv) A similar analysis is carried out for Ni and EuO, using the linear-model parameters of Ho,[38] Menyuk,[22] and Høg and Johansson.[23] The discrepancy between experiment and theory at zero magnetic field is large ($\approx 50\%$) and demonstrates the inadequacy of this equation for Ni and EuO. This discrepancy was not apparent in previous comparisons,[38] since these considered the specific heat difference between zero field and finite field, and there the effect is much less pronounced.

(v) A "modified MLSG" equation is proposed, containing an additional parameter which may be determined by a fit to the specific heat on the critical isochore. We have determined parameters for this equation by fitting specific-heat data in Xe, CO_2, EuO, and Ni over a restricted temperature range. This equation can also be made consistent with *PVT* measurements on Xe and CO_2 and *MHT* measurements on Ni and EuO. It must be remarked, however, that in our work, unlike Ref. 4, no complete statistical analysis has been made with the modified MLSG equation, to find the best parameter values consistent with all the data.

(vi) Using the modified MLSG equation in the magnetic case, the specific heat is calculated at finite magnetic fields, and compared to the data of Connelly *et al.*[39] with only semiquantitative agreement.

(vii) The influence of the earth's magnetic field on the specific heat is estimated, and shown to be negligible for Ni, but significant for EuO in the range $|t| < 10^{-3}$. Unfortunately, presently available measurements[40,44] show other rounding mechanisms in this range. Data[39] in the rounded region very near T_c are also compared to calculated values in finite fields. It is found that a field of 2.5 Oe for Ni accounts for the shape of the spe-

TABLE VIII. Universal parameters of MLSG equation for FeF_2, ^{4}He λ point, and $RbMnF_3$.

System	α	β	E_2	A/A'	Γ/Γ'	$D\Gamma B^{\delta-1}$
FeF_2	0.135[a]	0.3395[b]	0.544	0.493[a]	3.48	1.33
^{4}He λ point	−0.015[c]	0.368[b]	1.045	1.065[c]	2.67	1.29
$RbMnF_3$	−0.135[d]	0.384[b]	2.69	1.46[d]	1.62	1.16

[a]Reanalysis of specific-heat data of M. B. Salamon and A. I. Kushima [AIP Conf. Proc. 5, 1269 (1971)] with the constraint $Q=0$.
[b]From ϵ expansion, Ref. 28, with $\epsilon=1$.
[c]Reference 11.
[d]Reference 31 (reanalysis of original data in Ref. 42).

cific-heat singularity in a semiquantitative way.

ACKNOWLEDGMENTS

We wish to thank G. Ahlers for helpful discussions throughout the course of this work. We are also indebted to J. M. H. Levelt Sengers and J. A. White for sending us copies of their papers prior to publication. We also thank D. E. Mapother for the use of his original Ni specific-heat data in a magnetic field.

APPENDIX A: CRITICAL EXPONENTS AND AMPLITUDES

We use the conventional notation[7] for exponents and amplitudes:

$$M=\Delta\rho=B(-t)^{\beta}, \quad t<0, \quad \rho=\rho_c, \; H=0 \tag{A1}$$

$$\chi=\Gamma t^{-\gamma}, \quad t>0, \quad \rho=\rho_c, \; H=0 \tag{A2}$$

$$\chi=\Gamma'(-t)^{-\gamma'}, \quad t<0, \quad \rho=\rho_c, \; H=0 \tag{A3}$$

$$C_V=C_M=C_H=(A/\alpha)t^{-\alpha}+C_B, \quad t>0, \quad \rho=\rho_c, \; H=0 \tag{A4}$$

$$C_\mu=C_H=(A'/\alpha')(-t)^{-\alpha'}+C_B', \quad t<0, \quad \rho=\rho_c, \; H=0 \tag{A5}$$

$$H=DM|M|^{\delta-1}, \quad t=0, \tag{A6a}$$

$$\Delta\mu=D\Delta\rho|\Delta\rho|^{\delta-1}, \quad t=0, \tag{A6b}$$

$$t\equiv(T-T_c)/T_c, \tag{A7}$$

$$\Delta\rho=\rho-\rho_c. \tag{A8}$$

According to scaling[17,7] we have an equation of state of the form

$$\Delta\mu=\Delta\rho|\Delta\rho|^{\delta-1}h(x), \tag{A9a}$$

$$H=M|M|^{\delta-1}h(x), \tag{A9b}$$

$$x\equiv t|\Delta\rho|^{-1/\beta}=t|M|^{-1/\beta}. \tag{A10}$$

The scaling assumption (A9) implies[17,7] exponent relations

$$2-\alpha=\beta(\delta+1)=2\beta+\gamma, \tag{A11}$$

$$\gamma=\gamma', \tag{A12}$$

$$\alpha=\alpha'. \tag{A13}$$

We shall moreover assume

$$B_0=B_0', \tag{A14}$$

where $B_0\equiv C_B(t=0)$ and $B_0'\equiv C_B'(t=0)$.

APPENDIX B: DIMENSIONLESS AND SCALED UNITS

All quantities are expressed in terms of dimensionless units.

For fluids, the density is in units of $\rho_N\equiv\rho_c$, the chemical potential in units of $\mu_N\equiv P_c/\rho_c$, the specific heat (per unit mass) in units of $P_c/T_c\rho_c$. In order to obtain the specific heat per mole one multiplies the dimensionless specific heat by

$$C_N\equiv(P_c w/T_c\rho_c)\times10^{-7}\ \text{J mole}^{-1}\,\text{K}^{-1}, \tag{B1}$$

where w is the molecular weight. We shall use the same notation for the dimensionless and dimensioned quantities. In Ref. 4 the dimensionless quantities are denoted by a star [e.g., $\Delta\rho^*=(\rho-\rho_c)/\rho_c$].

For magnets, we measure the field H in units of[37]

$$H_N=k_BT_c/Sg\mu_B, \tag{B2}$$

(where S is the spin, g the g factor, and μ_B the Bohr magneton), and the magnetization (per mole) in units of

$$M_N=NSg\mu_B, \tag{B3}$$

where N is Avogadro's number. Then the specific heat (per mole) turns out to be in units of

$$C_N^{\text{mag}}=(H_NM_N/T_c)\times10^{-7}=R, \tag{B4}$$

R being the gas constant in J mole^{-1}K^{-1}.

To go from the dimensionless variables H, M, t, $\Delta\rho$, $\Delta\mu$, and C, to the "universal variables" $\tilde{H}$, $\tilde{M}$, $\tilde{t}=t$, $\Delta\tilde{\rho}$, $\Delta\tilde{\mu}$, and $\tilde{C}$, we must scale x by

$$x_0\equiv B^{-1/\beta}, \tag{B5}$$

and $h(x)$ by

$$h_0\equiv h(x=0), \tag{B6}$$

i.e.,

$$\tilde{h}(\tilde{x})=\tilde{h}(x/x_0)=h_0^{-1}h(x). \tag{B7}$$

Then M amd $\Delta\rho$ are scaled by

$$\rho_0=M_0\equiv x_0^{-\beta}, \tag{B8}$$

H and $\Delta\mu$ are scaled by

$$\mu_0 = H_0 \equiv h_0 x_0^{-\beta\delta}, \tag{B9}$$

and the specific heat is scaled by

$$C_0 \equiv h_0 x_0^{\alpha-2}. \tag{B10}$$

The scale factors are related to the critical amplitudes by the relations

$$B = x_0^{-\beta}, \tag{B11}$$

$$D = h_0, \tag{B12}$$

$$\Gamma = \lim_{x\to\infty} x^\gamma h(x) = x_0^\gamma h_0^{-1} \lim_{\tilde{x}\to\infty} \tilde{x}^\gamma \tilde{h}(\tilde{x}), \tag{B13}$$

$$\Gamma' = \beta x_0^{\gamma-1} h'(-x_0) = \beta h_0^{-1} x_0^\gamma \tilde{h}'(-1). \tag{B14}$$

From Eqs. (B11)–(B14) it is seen that Γ/Γ' and $D\Gamma B^{\delta-1}$ are indeed independent of the scale factors x_0 and h_0. Table VII lists the scale factors and normalization constants we use for the modified *MLSG* analysis of CO_2, Xe, Ni, and EuO.

APPENDIX C: THERMODYNAMIC FUNCTIONS IN THE SCALING REPRESENTATION

The functions $h(x)$ and $\tilde{h}(\tilde{x})$ have a power-series expansion[7] about $x=0$,

$$h(x) = \sum_{n=0}^{\infty} h_n x^n, \tag{C1}$$

$$\tilde{h}(\tilde{x}) = \sum_{n=0}^{\infty} \tilde{h}_n \tilde{x}^n, \tag{C2}$$

and for large x,

$$h(x) = \sum_{n=0}^{\infty} \eta_{n+1} x^{\gamma-2n\beta}, \tag{C3}$$

$$\tilde{h}(\tilde{x}) = \sum_{n=0}^{\infty} \tilde{\eta}_{n+1} \tilde{x}^{\gamma-2n\beta}. \tag{C4}$$

The free energy is given by (in magnetic notation)

$$A(M,T) = A_B(M,T) + |M|^{\delta+1} a(x), \tag{C5}$$

with

$$-xa'(x) + (2-\alpha)a(x) = \beta h(x). \tag{C6}$$

The solution of this equation, analytic near $x=0$, is[7]

$$a(x) = \beta\left(\frac{h_0}{2-\alpha} + \frac{h_1 x}{1-\alpha} + \frac{h_2 x^2}{-\alpha} - x|x|^{1-\alpha}\int_0^x dy\, |y|^{\alpha-3}[h(y) - h_0 - h_1 y - h_2 y^2]\right). \tag{C7}$$

As mentioned in Sec. III, this expression is equivalent to Eq. (22) of Griffiths[7] for $\alpha > 0$, and it is the correct generalization to the case $\alpha < 0$. The function $A_B(M,T)$ is assumed for simplicity to be an analytic function of T, and independent of M, although in a more accurate treatment[8,9] it would also contain singular correction terms. The thermodynamic functions may now be written as

$$\chi^{-1} = |M|^{\delta-1}[\delta h(x) - \beta^{-1} x h'(x)], \tag{C8}$$

$$\begin{aligned} C_M &= C_B - |M|^{-\alpha/\beta} a''(x) \\ &= C_B - |M|^{-\alpha/\beta}[x^{-2}(1-\alpha)(2-\alpha)a(x) - x^{-2}(1-\alpha)\beta h(x) - x^{-1}\beta h'(x)], \end{aligned} \tag{C9}$$

$$C_H = C_M + |M|^{-\alpha/\beta}[h'(x)]^2[\delta h(x) - \beta^{-1} x h'(x)]^{-1} \tag{C10}$$

$$= C_B - |M|^{-\alpha/\beta}\{x^{-2}(1-\alpha)(2-\alpha)a(x) - x^{-2}(1-\alpha)\beta h(x) - x^{-1}\beta h'(x) - [h'(x)]^2[\delta h(x) - \beta^{-1} x h'(x)]^{-1}\}, \tag{C11}$$

where $C_B = -T\partial^2 A_B/\partial T^2$. For fluids C_M corresponds to C_V and C_H to C_μ. In deriving Eqs. (C9–C11) we have dropped a factor $(1+t)$ multiplying $|M|^{-\alpha/\beta}$, and included the correction term $t|M|^{-\alpha/\beta}$ in the background term C_B. From Eqs. (C10) and (C7) we may calculate the coefficients A and A' defined in Eqs. (A4) and (A5). The results are

$$A = \beta\alpha(1-\alpha)(2-\alpha)\int_0^\infty dy\, y^{\alpha-3}[h(y) - h_0 - h_1 y - h_2 y^2], \tag{C12}$$

$$A' = -\beta\alpha(1-\alpha)(2-\alpha)\left(\frac{h_0}{2-\alpha} - \frac{h_1}{1-\alpha} - \frac{h_2}{\alpha} + \int_0^{-1} dy\, |y|^{\alpha-3}[h(y) - h_0 - h_1 y - h_2 y^2]\right). \tag{C13}$$

We do not use the expressions in Table II of Ref. 7, since they apply only for $\alpha > 0$. Equations (C12) and (C13) clearly also hold using "universal variables" $\tilde{h}(\tilde{x})$, with coefficients $\tilde{h}_n$ [see Eq. (C2)]. From Eq. (C10) we may easily find the specific-heat coefficient along the critical isotherm [see Eq. (3.18)],

$$A_H = 2\beta\alpha^{-1} h_2 + (h_0\delta)^{-1} h_1^2. \tag{C14}$$

APPENDIX D: MLSG AND MODIFIED MLSG EQUATIONS

Let us define the function

$$h(x) = e_1\left(\frac{x+x_0}{x_0}\right)\left[1 + e_2\left(\frac{x+x_0}{x_0}\right)^q\right]^p, \tag{D1}$$

$$\tilde{h}(\tilde{x}) = (1+e_2)^{-p}(\tilde{x}+1)[1 + e_2(1+\tilde{x})^q]^p. \tag{D2}$$

The MLSG equation corresponds to

$$e_1 = E_1, \tag{D3}$$

$$e_2 = E_2, \tag{D4}$$

$$p = (\gamma-1)/2\beta, \tag{D5}$$

$$q = 2\beta, \tag{D6}$$

and the modified MLSG equation is defined with

e_1, e_2, and

$$p \equiv (\gamma - 1)/2\beta e_3, \tag{D7}$$

$$q \equiv 2\beta e_3. \tag{D8}$$

For both equations, the quantities necessary to calculate the specific heat (which we shall express in universal variables) are $\tilde{h}_0 = 1$, $\tilde{h}_1$, $\tilde{h}_2$, $\tilde{h}'(\tilde{x})$, $\tilde{h}''(\tilde{x})$, h_0, and x_0. From Eq. (D2) we find

$$\tilde{h}'(\tilde{x}) = (1+e_2)^{-p}[1+e_2(1+\tilde{x})^q]^{p-1}[1+e_2(1+pq)(1+\tilde{x})^q], \tag{D9}$$

$$\tilde{h}''(\tilde{x}) = (1+e_2)^{-p} e_2 pq[1+e_2(1+\tilde{x})^q]^{p-2}(1+\tilde{x})^{q-1} \times[1+q+e_2(1+\tilde{x})^q(pq+1)], \tag{D10}$$

$$\tilde{h}_1 = (1+e_2)^{-1}[1+e_2(1+pq)], \tag{D11}$$

$$\tilde{h}_2 = \tfrac{1}{2} e_2 pq(1+e_2)^{-2}[1+q+e_2(1+pq)], \tag{D12}$$

$$\tilde{h}_0 = e_1(1+e_2)^p. \tag{D13}$$

The integrations in Eqs. (C12) and (C13) were performed numerically, with the portion near $y=0$ integrated analytically using the expansion (C2), because of the singular nature of the integrand.

APPENDIX E: PARAMETRIC REPRESENTATION AND THE "LINEAR MODEL"

In the parametric representation we define the variables r and θ by the relations

$$H = a\theta(1-\theta^2)r^{\beta\delta}, \tag{E1}$$

$$t = (1-b^2\theta^2)r. \tag{E2}$$

Then the equation of state has the form

$$M = K(\theta)r^\beta. \tag{E3}$$

General expressions for the thermodynamic functions have been given by Schofield,[18] but they are not simple unless $K(\theta)$ has a simple form. We shall discuss the linear model[5]

$$K(\theta) = k\theta. \tag{E4}$$

Corresponding to the universal variables $\tilde{h}$ and $\tilde{x}$, we may choose the scale of H and M such that

$$\left(\frac{dH}{d\theta}\right)_{\theta=0} = 1 \tag{E5}$$

and

$$\left(\frac{dM}{d\theta}\right)_{\theta=0} = 1. \tag{E6}$$

This means that we use $\tilde{H} \equiv H/a = H/H_0$, and $\tilde{M} = M/k = M/M_0$. Since in the parametric representation the universal variables are linearly related to the usual dimensionless variables, it is very simple to pass from one set to the other, and we shall not write down the formulas explicitly.

For the linear model the free energy may be obtained analytically[5] and an algebraic expression written down for the specific heat.[14] For completeness, we reproduce the main formulas of Ref. 14 below: The singular part of the free energy is

$$A_s = f(\theta)r^{2-\alpha}, \tag{E7}$$

$$f(\theta) = f_0 + f_2\theta^2 + f_4\theta^4, \tag{E8}$$

$$f_0 = (ak/2b^4)[\delta - 3 - b^2\alpha(\delta-1)][(\delta+1)(\alpha-1)\alpha]^{-1}, \tag{E9}$$

$$f_2 = -(ak/2b^2)[\beta(\delta-3) - b^2\alpha(1-2\beta)][\alpha(\alpha-1)]^{-1}, \tag{E10}$$

$$f_4 = -\tfrac{1}{2}ak(1-2\beta)\alpha^{-1}. \tag{E11}$$

The specific heat is given by

$$C_H - C_B = c_h(\theta)r^{-\alpha}, \tag{E12}$$

$$c_h(\theta) = \left(\frac{ak}{2b^4\alpha(1-\alpha)}\right) \times\left(\frac{(1-\alpha)(1-3\theta^2)(\bar{s}_0+\bar{s}_2\theta^2) - 2\beta\delta\theta^2\bar{s}_2(1-\theta^2)}{1+(2b^2\beta\delta-3-b^2)\theta^2 - b^2(2\beta\delta-3)\theta^4}\right), \tag{E13}$$

$$\bar{s}_0 = \beta(\delta-3) - b^2\beta\alpha(\delta-1), \tag{E14}$$

$$\bar{s}_2 = (\alpha-1)(\delta-3)\beta b^2, \tag{E15}$$

$$C_M - C_B = c_m(\theta)r^{-\alpha}, \tag{E16}$$

$$c_m(\theta) = \left(\frac{ak}{2b^4\alpha(1-\alpha)}\right)\left(\frac{(1-\alpha)\bar{s}_0 + (1-\alpha-2\beta)\bar{s}_2\theta^2}{1-b^2(1-2\beta)\theta^2}\right) \tag{E17}$$

where C_B is a background term which we here take to be a smooth function of t. The amplitudes are

$$A = \alpha c_h(\theta=0), \tag{E18}$$

$$A' = \alpha c_h(\theta=1)(1-b^2)^\alpha. \tag{E19}$$

The inverse susceptibility is

$$\chi^{-1} = (a/k)X(\theta)r^\gamma, \tag{E20}$$

$$X(\theta) = \frac{1-[3+b^2(1-2\beta\delta)]\theta^2 + b^2\theta^4(3-2\beta\delta)}{1-b^2(1-2\beta)\theta^2}, \tag{E21}$$

whence

$$\Gamma/\Gamma' = 2(b^2-1)^{1-\gamma}[1-b^2(1-2\beta)]^{-1}. \tag{E22}$$

Finally it may be easily seen that

$$D\Gamma B^{\delta-1} = b^{\delta-3}(b^2-1)^{1-\gamma}. \tag{E23}$$

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