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A Proposal for Corrections to Thermodynamic Scaling¹⁾

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Abstract. Application of the scaling hypothesis has been highly successful in the immediate vicinity of the critical point. The determination of critical exponents from experiments usually incorporates a wide range of temperature so that the scaling theories would have to be generalized to a larger neighborhood around the critical point. We propose such an extension which is consistent with available experimental data on the structural phase transformations in SrTiO_3 , LaAlO_3 and the order-disorder transitions in MnF_2 . It is shown through this scheme that *two* critical exponents can be deduced from given data on the temperature dependence of the order parameter.

I. Introduction

In recent years there has been a great deal of effort, both theoretical and experimental, towards understanding and clarifying the scaling hypothesis [1]–[3] of Widom-Kadanoff-Domb and the resulting scaled equation of state [4]. This description, while it has been very successful, is strictly applicable only in the immediate neighborhood of the critical point.

The underlying assumption of the scaling hypothesis is that the free energy may be regarded as a homogeneous function of the thermodynamic variables. A first-principle knowledge of the free energy is known only for the classical models and the Bose gas [5]. Recently, Green, Cooper and Levelt-Sengers [6] have proposed a generalization of the parametric representation of the free energy introduced by Schofield [7] and Josephson [8] with the view to extending the domain of applicability of the conventional scaling theories. In this work we propose an alternative generalization.

Our starting point is the assumption that the free energy is an analytic function of two variables everywhere in the vicinity of the critical point except on the phase boundary. This implies that a double Taylor series expansion in the two variables exists and is absolutely convergent about any non-singular point [4]. We shall further assume that the free energy can be decomposed into a 'regular' and a 'singular' part. These two assumptions also seem to underlie the scaling theories [4], [9], [10].

We expand the free energy about the critical isochore (not the critical point). On such a curve the free energy is a function of only one variable. We argue, in the

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spirit of the above assumption, the coefficients of this expansion may be described as a sum of a 'regular' and a part that becomes 'singular' at the critical point. The leading term of the 'singular' part of the coefficients in an expansion about the critical point describes the leading critical behaviour of a corresponding thermodynamic quantity. The remaining terms of such an expansion, together with the regular part of these coefficients, constitute the correction terms as one goes away from the critical point. While it is true, in principle, that there are two species of correction terms we shall argue that the important ones are those arising from the regular part.

In section II we carry out this scheme for a magnet. We generalize the scaled equation of state, the expression for the susceptibility and the spontaneous magnetization (the order parameter) in the neighborhood of the critical point. We identify the leading term in each expression with that given by simple scaling. An important result is that the corrections to the leading temperature dependence of the order parameter close to T_c , are determined by an additional critical exponent, namely, $\gamma^- \equiv \gamma'$. This suggests that from given data on the temperature dependence of the order parameter, close to T_c , *two* critical exponents can be determined, namely, $\beta^- \equiv \beta$ and γ' . In section III we apply this scheme to the experimental data of SrTiO_3 [11], LaAlO_3 [11], MnF_2 [12] and determine β and γ' , as well as the amplitude of the leading and the first few correction terms. Our results (β , γ' , amplitude of the leading term) turn out to be consistent with the experimental information available.

II. Formalism

Let $A(T, M)$ be the free energy per spin of a ferromagnet with the properties

$$H = \left(\frac{\partial A}{\partial M} \right)_T, \quad S = - \left(\frac{\partial A}{\partial T} \right)_M, \quad (1)$$

where H is the external magnetic field, M is the average magnetization per spin in the direction of H , S is the entropy per spin, and T the temperature. The usual assumption that $A(M, T)$ is convex-downward for fixed T is made. This corresponds to the positivity of the isothermal susceptibility, χ_T ,

$$\frac{1}{\chi_T} = \left(\frac{\partial^2 A}{\partial M^2} \right)_T \geq 0. \quad (2)$$

The spontaneous magnetization, M_s , is the solution of

$$\left(\frac{\partial A}{\partial M} \right)_T = 0. \quad (3)$$

The curve of spontaneous magnetization in the M - T plane is shown in the Figure. Beneath this phase boundary curve is the 'two-phase' region, and above this curve lies the 'one-phase' region.

One of the basic assumptions about the thermodynamic free energy, $A(M, T)$, is that it is an analytic function of *both* arguments together in the vicinity of the critical

point except on the phase boundary [4]. Such an assumption implies that given any point (M_0, T_0) not on the phase boundary, the series

$$A(M, T) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \alpha_{ij} (M - M_0)^{2i} (T - T_0)^j \quad (4)$$

converges for $|M - M_0|$ and $|T - T_0|$ smaller than some positive constants Δ_M and Δ_T , respectively, which will depend on the point (M_0, T_0) . It has been shown [4, 13] that scaling obtains with an additional assumption that the free energy is a 'homogeneous' function. One is actually interested in describing the free energy at and around

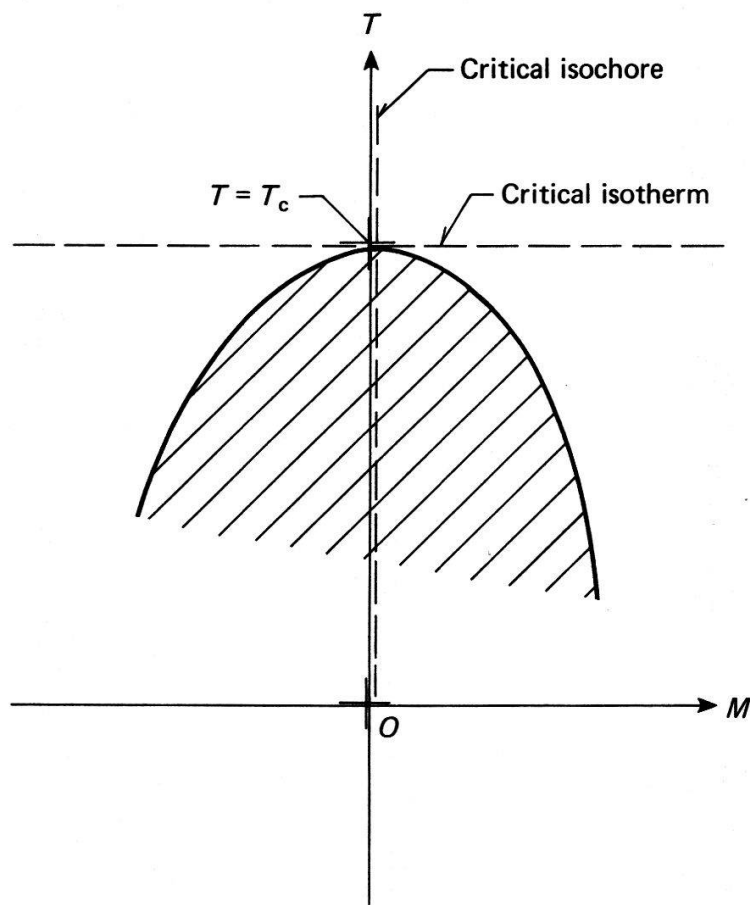


Figure 1

The spontaneous magnetization phase boundary. The two-phase region is shaded.

the critical point. However, the free energy cannot be directly expanded about the critical point because, according to what we have stated above, the critical point is a singular point in both variables. We can avoid this difficulty by expanding about a point on the critical curves ($M = 0$ and $T = T_c$) excluding the critical point where the free energy is singular in only one variable. Let us consider a point on the curve $M = 0$, or the curve $T = T_c$, far away from the critical point. We know that about this point the free energy may be expanded as follows:

$$A(M, |\epsilon|) = \sum_{n=0}^{\infty} \alpha_{2n}^{\pm} (|\epsilon|) M^{2n} \quad (5)$$

and

$$A(M, \epsilon) = \sum_{n=0}^{\infty} \alpha_n(M) |\epsilon|^n, \quad (6)$$

respectively. In equations (5) and (6), $\epsilon \equiv (T - T_c)/T_c$ and the \pm sign refer to $\epsilon \gtrless 0$. Consider, for example, the expansion about the line $M = 0$ [equation (5)]. (It must be remarked that in this expansion the magnetization variable always lies in the one-phase region; for in the two-phase region the free energy is a function of T only.) We shall argue that as we approach the critical point along this curve, the coefficients $\alpha_{2n}(\epsilon)$ may be decomposed into a part that is 'regular' and a part that is 'singular' at the critical point, respectively. This amounts to assuming that at the critical point the free energy may be written as a sum of a 'regular part' and a 'singular part'. This assumption also seems to be implicit in conventional scaling theories [9], [10]. We shall therefore write

$$\alpha_{2n}(|\epsilon|) = \bar{\alpha}_{2n}(|\epsilon|) + \tilde{\alpha}_{2n}(|\epsilon|) \quad (7)$$

where $\bar{\alpha}$ is the regular part and $\tilde{\alpha}$ is the singular part. Since by definition $\bar{\alpha}$ is regular at $T = T_c$ we know that the Taylor series

$$\bar{\alpha}_{2n}^{\pm}(|\epsilon|) = \sum_{i=1}^{\infty} \bar{b}_{2n,i}^{\pm} \cdot |\epsilon|^i \quad (8)$$

exists and is absolutely convergent provided $|\epsilon|$ is smaller than a positive constant. Let us now turn to the 'singular part', $\tilde{\alpha}(|\epsilon|)$. Following Coopersmith we shall assume that these coefficients, and consequently the free energy, have at most algebraic singularities [14]. This means that in the neighborhood of the singular point, in this case $\epsilon = 0$, such an algebraic function may be expanded as follows [15]:

$$\tilde{\alpha}_{2n}(\epsilon) = \sum_{j=r_n}^{\infty} \tilde{b}_{2n,j} |\epsilon|^{j/N_n}. \quad (9)$$

Here N_n is the degree of the algebraic function $\alpha_{2n}(\epsilon)$ and r_n is a positive or a *finite* negative integer. (In these defining equations we have suppressed the \pm signature of these coefficients so as not to obscure the point. We shall resume using them when necessary.) The leading term of each coefficient $\tilde{\alpha}_{2n}$ (viz., $j = r_n$) determines the (leading) critical exponent for the corresponding power of M which represents a particular thermodynamic quantity [14]. The remaining terms of expansion (9), together with the regular part [equation (8)], we shall call, in anticipation, the correction terms to the coefficient $\alpha_{2n}(\epsilon)$.

Let us now return to expansion (5). With the aid of the defining equation (1) we obtain for the magnetic field,

$$\frac{H}{M} = \sum_{n=1}^{\infty} 2n \alpha_{2n}^{\pm}(|\epsilon|) M^{2(n-1)}. \quad (10)$$

In order to introduce the concept of 'correction terms' it is convenient at this point to introduce the reduced variables

$$\begin{aligned} m &= |\epsilon|^{-\beta^-} M \\ h &= |\epsilon|^{-\beta^- - \gamma^{\pm}} H. \end{aligned} \quad (11)$$

We can now rewrite the equation of state, viz., equation (10), as

$$\frac{h}{m} = \sum_{n=1}^{\infty} 2n \alpha_{2n}^{\pm}(|\epsilon|) |\epsilon|^{2\beta^-(n-1) - \gamma^{\pm}} m^{2(n-1)}. \quad (12)$$

In equations (11) and (12), β^- and γ^\pm are the critical exponents describing the asymptotic behavior of the temperature dependence of the spontaneous magnetization, M_s ,

$$M_s = M_0 |\epsilon|^{\beta^-} \quad (13)$$

and that of the zero-field susceptibility

$$\chi_T = \Gamma^\pm |\epsilon|^{-\gamma^\pm}. \quad (14)$$

It is an assumption of scaling theories that in equation (12)

$$\alpha_{2n}^\pm(|\epsilon|) \cdot |\epsilon|^{2\beta^-(n-1)-\gamma^\pm} = b_{2n}^\pm, \quad (15)$$

where the b_{2n} 's are constants [4]. With this assumption equation (12) immediately leads to the 'scaled equation of state'

$$\begin{aligned} \frac{h}{m} &= K^\pm(m) \\ &= \sum_{n=1}^{\infty} 2n b_{2n}^\pm m^{2(n-1)}. \end{aligned} \quad (16)$$

Equation (16) says that a plot of h versus m consists of two branches (one for $T > T_c$, and one for $T < T_c$). These two branches must clearly converge asymptotically (as $T \rightarrow T_c$) as the free energy itself is continuous across T_c [16]. Since along this asymptote we must obtain the equation of state on the critical isotherm, viz.,

$$M \sim H^{1/\delta} \quad (17)$$

it follows that in the limit of large m

$$K^\pm(m) \sim m^{\delta-1} \quad (18)$$

and that

$$\delta = 1 + \frac{\gamma^\pm}{\beta^-}, \quad (19)$$

[see equation (11)]. The scaled equation of state (16) has been very successful in reducing the data taken on many different isotherms (close to T_c) to a single plot consisting of two branches [16]. However, such a scaling hypothesis can only be applied very close to the critical point. In what follows we shall show how one may correct for this in the sense of extending the domain of applicability of the equation of state.

We shall now invoke our earlier assumption about the coefficients $\alpha_{2n}(\epsilon)$ in expansion (5) of the free energy, namely, that in the neighborhood of the critical point it may be written as a sum of regular and singular parts. Substituting equation (7) into equation (12) we obtain

$$\frac{h}{m} = \sum_{n=1}^{\infty} 2n [\bar{\alpha}_{2n}^\pm(|\epsilon|) + \tilde{\alpha}_{2n}^\pm(|\epsilon|)] |\epsilon|^{2\beta^-(n-1)-\gamma^\pm} m^{2(n-1)}. \quad (20)$$

Using expansions (8) and (9) for $\bar{\alpha}$ and $\tilde{\alpha}$, respectively, we get

$$\frac{h}{m} = \sum_{n=1}^{\infty} 2n \left[\sum_{i=1}^{\infty} \bar{b}_{2n,i}^\pm |\epsilon|^i + \sum_{j=r_n}^{\infty} \tilde{b}_{2n,j}^\pm |\epsilon|^{j/N_n} \right] |\epsilon|^{2\beta^-(n-1)-\gamma^\pm} m^{2(n-1)}. \quad (21)$$

We shall now use the fact that the term corresponding to $j = r_n$ in the second series inside the square bracket in equation (21) leads to the usual (leading) critical exponent [14]. Let us rewrite equation (21) in the form

$$\frac{h}{m} = \sum_{n=1}^{\infty} 2n \tilde{b}_{2n,r_n}^{\pm} \cdot m^{2(n-1)} |\epsilon|^{2\beta(n-1)-\gamma^{\pm} + \frac{r_n}{N_n}} \left[1 + \sum_{j=1}^{\infty} \frac{\tilde{b}_{2n,r_n+j}^{\pm}}{\tilde{b}_{2n,r_n}^{\pm}} |\epsilon|^{j/N_n} + \sum_{i=1}^{\infty} \frac{\bar{b}_{2n,i}^{\pm}}{\tilde{b}_{2n,r_n}^{\pm}} \cdot |\epsilon|^{i - \frac{r_n}{N_n}} \right]. \quad (21a)$$

According to what has been stated above, scaling must obtain if we neglect all except the first term in the bracket in equation (21a). It therefore follows that

$$2\beta^-(n-1) - \gamma^{\pm} = -\frac{r_n}{N_n}.$$

Equation (21a) can now be rewritten as

$$\frac{h}{m} = \sum_{n=1}^{\infty} 2n \tilde{b}_{2n,r_n}^{\pm} \cdot m^{2(n-1)} \left[1 + \sum_{j=1}^{\infty} \frac{\tilde{b}_{2n,r_n+j}^{\pm}}{\tilde{b}_{2n,r_n}^{\pm}} |\epsilon|^{j/N_n} + \sum_{i=1}^{\infty} \frac{\bar{b}_{2n,i}^{\pm}}{\tilde{b}_{2n,r_n}^{\pm}} |\epsilon|^{i+2\beta(n-1)-\gamma^{\pm}} \right]. \quad (22)$$

The second and third terms in parenthesis in equation (22) we call the *correction terms*. In this description there are two different kinds of correction terms. The first series in parenthesis in equation (22) represents the correction terms arising from the expansion of the 'singular part' of α_{2n} , and the second series represents the 'regular part' of α_{2n} [see equations (8) and (9)]. In principle, both types of correction terms should become important as we go away from the critical point. We shall now argue that the correction terms arising from the 'singular part' are less important than those arising from the 'regular part'. Coopersmith [14] has demonstrated (in the language of algebraic free energy) that in order to obtain reasonable values for the critical exponents one would have to assume that the free energy has a very large number of branches at the critical point (i.e., N_n is large). Consequently, the importance of the correction terms due to the singular part of α_{2n} is restricted to small ϵ values, and depends on the amplitudes ($\tilde{b}_{2n,r+1}^{\pm}/\tilde{b}_{2n,r}^{\pm}$), etc. However, the fact that one has been able to characterize the asymptotic behavior ($\epsilon \rightarrow 0$) in terms of a 'leading exponent' seems to indicate that these *amplitudes* must be small. Otherwise, given that N_n is usually large, it would have been meaningless to characterize the asymptotic behavior in terms of a 'leading' exponent (we know that such a characterization has been largely successful). In view of this we shall, in what follows, ignore these correction terms. The remaining correction terms are, then, due to the regular part of $\alpha_{2n}(\epsilon)$. We therefore rewrite equation (22) as

$$\frac{h}{m} \approx \sum_{n=1}^{\infty} 2n \tilde{b}_{2n,r_n}^{\pm} [1 + B_{2n}^{\pm}(|\epsilon|)] m^{2(n-1)}, \quad (23)$$

where

$$B_{2n}^{\pm}(|\epsilon|) = \sum_{i=1}^{\infty} \frac{\bar{b}_{2n,i}^{\pm}}{\tilde{b}_{2n,r_n}^{\pm}} |\epsilon|^{i+2\beta^-(n-1)-\gamma^{\pm}}. \quad (24)$$

To insure that the free energy exists at the critical point, we impose the condition that

$$\begin{aligned} \bar{b}_{2n,i}^{\pm} &\neq 0 \quad \text{if } i + 2\beta^-(n-1) - \gamma^{\pm} > 0 \\ &= 0 \quad \text{if } i + 2\beta^-(n-1) - \gamma^{\pm} \leq 0. \end{aligned} \quad (25)$$

In order to obtain from equation (23) expressions for the spontaneous magnetization and the susceptibility, etc., we would have to, in practice, truncate the series in m . Firstly, we know that the assumption of an analytic free energy in the one-phase region guarantees that this series is absolutely convergent. Moreover, the studies in Ni of Kouvel and Colmy [16] have shown that in the limit h/m tending to zero, this ratio is linear in m^2 . Physically, this limit corresponds to close proximity of the coexistence curve ($T < T_c, H \rightarrow 0$). Since we are interested precisely in this limit we shall truncate the series (23) after the $n = 2$ term. We thus obtain

$$\frac{h}{m} \approx 4\tilde{b}_{4,r_2}^- [1 + B_4^-(|\epsilon|)] [m^2 - m_s^2], \quad (26)$$

where

$$m_s^2 = \frac{M_s^2}{|\epsilon|^{2\beta^-}} = - \frac{\tilde{b}_{2,r_1}^- [1 + B_2^-(|\epsilon|)]}{2\tilde{b}_{4,r_2}^- [1 + B_4^-(|\epsilon|)]}. \quad (27)$$

m_s is the reduced spontaneous magnetization, related to M_s by equation (11). Similarly, we obtain for the zero-field isothermal susceptibility, using equations (2), (11), (23) and (26),

$$\begin{aligned} \frac{1}{\chi_T} &= 8m_s^2 \tilde{b}_{4,r_2}^- [1 + B_4^-(|\epsilon|)] |\epsilon|^{\gamma^-} \\ &= -4\tilde{b}_{2,r_1}^- [1 + B_2^-(|\epsilon|)] |\epsilon|^{\gamma^-}. \end{aligned} \quad (28)$$

Let us now return to equation (27) for M_s^2 . With the aid of equation (24) we rewrite the expression for the spontaneous magnetization in the form

$$M_s^2 = M_0^2 |\epsilon|^{2\beta^-} \left[\frac{1 + C_{2,2}^- |\epsilon|^{2-\gamma^-} + C_{2,3}^- |\epsilon|^{3-\gamma^-} + \dots}{1 + C_{4,1}^- |\epsilon|^{1+2\beta^--\gamma^-} + C_{4,2}^- |\epsilon|^{2+2\beta^--\gamma^-} + \dots} \right], \quad (29)$$

where

$$M_0^2 = - \frac{\tilde{b}_{2,\gamma^-}^-}{\tilde{b}_{4,\gamma^- - 2\beta^-}^-}, \quad C_{2,2}^- = \frac{\bar{b}_{2,2}^-}{\tilde{b}_{2,\gamma^-}^-}, \quad C_{4,1}^- = \frac{\bar{b}_{4,1}^-}{\tilde{b}_{4,\gamma^- - 2\beta^-}^-}, \quad \text{etc.} \quad (30)$$

In equation (29) the coefficient $C_{2,1}^-$ has been set equal to zero. This is consistent with our assertion, namely, equation (25) and for values $\beta^- \approx 1/3$, $\gamma^- \approx 4/3$. Equation (29) clearly demonstrates that, including the correction terms, the spontaneous magnetization is determined by two critical exponents, namely, β^- and γ^- . Consequently, from given data on $M_s(|\epsilon|)$ close enough to T_c , two exponents may be derived. Using the Rushbrooke inequality [17]

$$\alpha^- \geq 2(1 - \beta^-) - \gamma^- \quad (31)$$

we can then obtain a lower bound on α^- , the leading critical exponent of the zero-field specific heat.

We observe, however, that the correction terms of the susceptibility [equations (24) and (28)], do not involve any additional exponent.

III. Application and Comparison

Using some available experimental data on the temperature dependence of the order parameter we determined with the aid of equation (29) the critical exponents β^- , γ^- , the amplitude M_0 and some amplitudes of the correction terms.

In SrTiO_3 and LaAlO_3 we used the order-parameter measurements of Müller and Berlinger [11] on the structural phase transitions which occur at $T \approx 105^\circ\text{K}$ and $T \approx 797^\circ\text{K}$, respectively. The nature of these transitions was deduced by EPR measurements [18], [19]. The results showed clearly that below T_c the BO_6 octahedra are rotated with respect to the cube axes, with the sense of rotation alternating from cell to cell in all three directions. As a consequence, the rotation angle corresponds to the order parameter, and the susceptibility χ_T describes the mean-square deviation of the rotation angle. In MnF_2 we used the staggered magnetization measurements of Heller [12].

The results of the nonlinear least-square fit procedure are summarized in Table 1. (A brief outline of this procedure is given in the Appendix.) In this Table the lower bound of α^- has been calculated with the aid of the Rushbrooke inequality equation (31). For comparison with our fit, we have also fitted the formula of Green, Cooper and Levelt-Sengers [6], namely, equation (4b) in their paper,

$$M = M_0 |\epsilon|^{\beta^-} [1 + C_1 |\epsilon|^x + C_2 |\epsilon|^{2x} + \dots], \quad (32)$$

where

$$x = 1 - \alpha^- - \beta^- = \beta^- + \gamma^- - 1. \quad (33)$$

The results of this fit are also shown in Table 1. We observe that the correction term parameters are rather undetermined on the basis of equation (32) (GCLS) but well defined by using our expression [equation (29), SSS]. We also note that the SSS formula fits all the examples (with the same number of parameters) with a significantly smaller mean-square residual. We therefore conclude that the nature of correction terms as expressed in our formalism is more consistent with the experimental data. In SrTiO_3 and LaAlO_3 we varied four parameters. In MnF_2 , where more experimental data was available, five parameters were varied. In the course of this fitting procedure the following amplitudes of the correction terms turned out to be negligibly small: $C_{4,2}^-$ in SrTiO_3 , LaAlO_3 , and $C_{4,1}^-$ in MnF_2 .

Unfortunately, the available experimental data on the exponents listed in Table 1 is quite limited. A summary is given in Table 2. We observe that our results are consistent with direct measurements of these exponents.

From Table 1 it is seen that the corresponding exponents in SrTiO_3 and LaAlO_3 nearly coincide. This is consistent with the intuitive notion that critical exponents depend most strongly on the *dimensionality* of the system and rather less upon the details of the interactions. In fact, the exponents are very close to those of the planar spin model [21] ($\beta^- = 1/3$, $\gamma^- = 4/3$, $\alpha^- = 0$), which one expects to apply to the rotations of the BO_6 octahedra occurring in the (100) and (110) planes in SrTiO_3 and LaAlO_3 ,

Table 1

Critical exponents and amplitudes as obtained from the measured data on the temperature dependence of the order parameter with the aid of Eqs. (29) (SSS) and (32) (GCLS). $\Delta|\epsilon|$ denotes the temperature range of the data used in the fitting procedure

	SrTiO ₃ Fe ³⁺ - V ₀		LaAlO ₃		MnF ₂	
	SSS	GCLS	SSS	GCLS	SSS	GCLS
α^-	$\geq 0.06 \pm 0.14$	0.02 ± 0.3	$\geq 0.02 \pm 0.3$	0.1 ± 2	$\geq 0.07 \pm 0.17$	-0.1 ± 1.3
β^-	0.333 ± 0.005	0.335 ± 0.002	0.330 ± 0.008	0.334 ± 0.006	0.32 ± 0.01	0.29 ± 0.03
γ'	1.28 ± 0.15	1.3 ± 0.3	1.35 ± 0.3	1.2 ± 1.7	1.29 ± 0.17	1.5 ± 1.3
M_0	1.08	1.08	0.86	0.86	1.10 ± 0.06	1.0 ± 2
$C_{2,2}^- C_1$	1.4 ± 0.2	-0.14 ± 0.04	0.96 ± 0.2	0.15 ± 1	0.96 ± 0.17	0.5 ± 1
$C_{4,1}^- C_2$	0.62 ± 0.09	1.5 ± 0.5	0.2 ± 0.3	0.4 ± 2.3	—	-0.5 ± 4
$C_{4,2}^- C_3$	—	—	—	—	1.6 ± 0.4	—
Mean-square residual	$0.11 \cdot 10^{-2}$	$0.15 \cdot 10^{-2}$	$0.10 \cdot 10^{-2}$	$0.11 \cdot 10^{-2}$	$0.58 \cdot 10^{-3}$	$0.36 \cdot 10^{-2}$
T_c	105.15		797		67.34	
$\Delta \epsilon $	0 - 0.25		0 - 0.26		0 - 0.22	

respectively. As may be seen from Table 1 the corresponding amplitudes for SrTiO₃ and LaAlO₃ are significantly different. This is not too surprising, as one can anticipate that the amplitudes depend on the specific space group [13]. In this context we point out that SrTiO₃ is tetragonal, and LaAlO₃ trigonal.

In order to get a feeling for the importance of the various correction terms we display in Table 3 the contributions to the order parameter squared for MnF₂. For this purpose we rewrite equation (29) as

$$M_s^2 = M_0^2 |\epsilon|^{2\beta} + M_{2,2}^2 |\epsilon|^{2+2\beta-\gamma^-} - M_0^2 C_{4,1}^- |\epsilon|^{1+4\beta-\gamma^-} - M_0^2 C_{4,2}^- |\epsilon|^{2+4\beta-\gamma^-} = M_L^2 + M_{2,2}^2 + M_{4,1}^2 + M_{4,2}^2. \quad (34)$$

As already mentioned, due to the smallness of $C_{4,1}^-$ the contribution $M_{4,2}^2$ has been neglected. From Table 3 it is seen that in MnF₂ the correction terms contribute less than 10% for $|\epsilon| < 0.04$. The relative magnitude of the correction terms is of the same order in SrTiO₃ and LaAlO₃ for $|\epsilon| < 0.03$. The region where the correction terms are negligible (in the above sense) provides a measure of the 'critical region', where scaling may be assumed to be applicable. It is clear from the above considerations that in a given experiment, if it is possible to go well into the critical region, then one can obtain meaningful exponents by taking into account the leading terms only. If on the other hand the nature of the transition is such that the 'critical region' is small and most of the data pertains to outside of the critical region, then, according to what we have stated, comparison must be made only with a theory that includes correction terms.

IV. Summary

The critical point is a singular point of the free energy. The mathematical characterization of this singularity is believed to be the central problem in the theoretical understanding of second-order phase transitions. Lately, there have been several theoretical attempts [1]–[4] towards describing the free energy and the related thermodynamic functions in the 'critical region', and these have been largely successful.

Experimentally, however, the determination of the critical exponents is often hampered by the fact that it is very hard to make measurements sufficiently close to the critical point. Consequently, this makes comparison with theories difficult. In this paper we have attempted to generalize the so-called 'scaled' free energy. We have done this by adding to the free energy of the conventional scaling theories terms which are *regular* at T_c and which become significant as one goes away from the critical point. It was

Table 2

Experimentally deduced values of critical exponents and amplitudes

	SrTiO ₃ Fe ³⁺ - V ₀	LaAlO ₃	MnF ₂
β^-	0.33 ± 0.02 [11]	0.33 ± 0.02 [11]	0.333 ± 0.003 [12]
γ^-	—	—	1.32 ± 0.06 [20]
M_0	—	—	1.2 ± 0.004 [12]

demonstrated in Section II that the structure of these added (regular) terms to the free energy is such that the correction terms to the leading behavior of the order parameter involves an additional exponent, viz., the leading critical exponent of the isothermal susceptibility.

It should be remarked here that even though we have confined our discussion to a magnet, the basic prescription of Section II, viz., that one may extend the domain of validity of scaling theories by adding to the free energy (regular) correction terms,

Table 3

Contributions to the order parameter squared from the first two non-negligible correction terms as a function of $|\epsilon|$ for MnF₂ [Eq. (34)]

$ \epsilon $	M_L^2	$M_{2,2}^2$	$M_{4,2}^2$	M_s^2	M_s^2 exp
0.00015	0.00444	0.00001	0	0.00445	0.00407
0.00020	0.00552	0.00001	0	0.00553	0.00508
0.00043	0.00880	0.00004	0	0.00884	0.00833
0.00199	0.02332	0.00028	-0.00001	0.02359	0.02251
0.00344	0.03304	0.00058	-0.00003	0.03359	0.03218
0.00733	0.05337	0.00160	-0.00012	0.05485	0.05457
0.01488	0.08358	0.00413	-0.00047	0.08722	0.08705
0.02986	0.13000	0.01051	-0.00186	0.13854	0.13907
0.04079	0.15843	0.01597	-0.00343	0.17070	0.17118
0.08615	0.25451	0.04349	-0.01503	0.28138	0.28124
0.15865	0.37485	0.09859	-0.05018	0.41754	0.41695
0.19931	0.43320	0.13386	-0.07874	0.47984	0.48177

should be applicable, in principle, to other systems as well. We observe that in equation (4) we have allowed only even powers of M (the order parameter). This special symmetry consideration for a magnet is dictated by time reversal symmetry in the absence of an external magnetic field. Also, in discussing structural phase transitions the concept of a free energy which is even in the order parameter is the appropriate one. If we were dealing with a liquid, for example, one would have to include both even and odd powers of the order parameter in the expansion of the free energy [see equation (4)]. An appropriate generalization of Section II for this case should, in principle, be immediate. We

saw [equation (26)] that in order to obtain an explicit expression for the order parameter we had to truncate the series given by equation (23). For the case under consideration the justification for such a truncation was derived from empirical facts [16]. At this point we have not been able to give a general justification for such a truncation for all systems.

We have applied the theory developed here to structural phase transitions in SrTiO_3 , LaAlO_3 , and MnF_2 and have been able to obtain two critical exponents (β and γ^-) from the measurements of the order parameter. The results are displayed in Tables 1 and 2. Recently, there has been another attempt in the same direction due to Green, Cooper and Levelt-Sengers [6]. They view the important corrections to the free energy as arising from other singular terms. We have applied their formalism to the systems we have discussed, and the results are also given in Table 1. We conclude that at least for the phase transitions considered by us, the nature of the correction terms as expressed in our formalism appears to be more consistent with the experimental data. Finally, it was shown (Table 3) that the magnitude of the correction terms provides some insight into the extent of the 'critical region', where scaling is applicable.

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Appendix

We think it is worth while sketching the principles underlying the non-linear least-square fit procedure. We assume that the statistical errors of the experimental data are randomly distributed. To get a unique distribution of these errors with the variance δ^2 we weight the influence of each measured value with a weight G_i . In the spirit of the statistical theory, the variance of each measured point, δ_i^2 , has to be multiplied with G_i in order to get a unique variance δ^2 . Due to the fact that the number of unknowns G_i is one less than the number of measured points we can choose δ^2 arbitrarily, for example, equal to one:

$$\delta^2 = G_i \delta_i^2 = 1 \quad (\text{A.1})$$

therefore

$$G_i = \frac{1}{\delta_i^2}. \quad (\text{A.2})$$

Unfortunately, error estimates are rarely given in the tabulated experimental data. However, we can make a rough estimate by assuming that all measured points have the same uncertainty. In this case the common variance cannot be normed and we have to estimate it by the fitting procedure. This amounts to choosing a set of functions $\phi(\alpha_1, \dots, \alpha_n; x_i)$ (α_i : parameters; x_i : variable, n : number of parameters), whose square of the averaged residual, $\rho_{\phi}^2(\text{fit})$, defined in (A.3) is equal to the weighted variance δ^2 of the experimental data,

$$\rho_{\phi}^2 = \frac{\sum_{i=1}^m \rho_i^2}{m-n} = \frac{\sum_{i=1}^m G_i (f_i - \phi)^2}{m-n}, \quad (\text{A.3})$$

$$\rho_{\phi}^2(\text{fit}) = \delta^2. \quad (\text{A.4})$$

Here f_i denotes the measured value and m the number of measured points.

According to a theorem of statistics [22] ρ_ϕ^2 cannot be less than δ^2 , and $\rho_{\phi(\text{fit})}^2$ is the least square of the averaged residuals. From the physical point of view not all functions ϕ have a physical meaning. Therefore each function describing a physical model has in general a mean-square residual ρ_ϕ^2 , which is greater than the variance squared δ^2 ,

$$\rho_\phi^2 > \delta^2. \quad (\text{A.5})$$

If the mean-square residual, as obtained with one physical model, is significantly smaller than that obtained with another model, we can conclude that the first-mentioned model is more consistent with experiment.

We observe that equation (28) is nonlinear in the parameters. In order to find in this case the minimal 'mean square of the residual', ρ^2 , we used in the first steps the gradient method described in Ref. [23]. Before reaching the minimum we changed to the so-called full matrix calculation [22]. In this region the surface of the mean-square residual (as a function of the parameters) can be approximated by a hyper-paraboloid. In this case the points of the standard deviations of all linear combinations of the parameters lie on a hyper-ellipse. To find the external points of this surface with respect to the parameters α_i we have to multiply the standard deviation δ with the square-root of the diagonal elements of the inverse matrix of the normal equation [22],

$$\delta_{\alpha_i} = \delta \sqrt{e_{ii}}. \quad (\text{A.6})$$

Since equation (28) does not satisfy equation (A.4) we tried to satisfy this condition with a further fitting procedure. The new function for ϕ , namely, ψ is a polynomial of degree L in the variables x_i :

$$\rho_{\psi,\phi}^2 = \frac{\sum_{i=1}^m (\rho_i - \psi(x_i))^2}{m - L} \cdot \frac{m}{m - n}. \quad (\text{A.7})$$

The degree L was chosen in such a way that $\rho_{\psi,\phi}^2$ has a minimum. With this condition and equation (A.4) we shall assume

$$\rho_{\psi,\phi}^2 \approx \delta^2. \quad (\text{A.8})$$

Substituting this value of δ into equation (A.6) we obtain for the uncertainty in the parameters

$$\delta_{\alpha_i} = \rho_{\psi,\phi} \sqrt{e_{ii}}. \quad (\text{A.9})$$

From this equation and (A.5) it follows that the number of parameters which we can meaningfully fit is determined by the inequality

$$\rho_{\psi,\phi}^2 < \rho_\phi^2. \quad (\text{A.10})$$

Since the left-hand side of this inequality is determined by the accuracy of the experimental data, and the right-hand side by the number of parameters, the above criterium does in fact show that the number of parameters (that can be meaningfully fitted) is related to the accuracy of the experimental data.

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