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Scaling Relations for Critical Exponents of Surface Properties of Magnets

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The critical behavior of the surface properties of magnets is discussed. A homogeneity assumption for the free energy, involving a new exponent ϕ_1 to scale the surface field, is introduced. New exponent relations are derived for the surface exponents. These are satisfied for the two-dimensional Ising model, the spherical model, and mean-field theory. The existing estimates for the three-dimensional Ising model, however, appear to be possibly inconsistent.

Considerable interest, both theoretical[1-3] and experimental,[4] has been shown recently in the critical behavior of magnetic systems with free surfaces. The surface quantities of interest are most conveniently defined[1] if we consider a spin system on a lattice[5] which is infinite in $d' = d-1$ dimensions but has $n(<\infty)$ "layers" in the dth dimension; the first and nth layers forming free surfaces. If $F(n, h, h_1, T)$ is the free energy (per spin) of this system in the presence of a uniform *bulk magnetic field* h and a *surface field*[6] h_1, then as $n\to\infty$, with h, h_1, and T fixed we expect[1] that

$$F(n, h, h_1, T) \approx F_\infty(h, T) + (2/n)F^\times(h, h_1, T) + \cdots , \quad (1)$$

where $F_\infty(h, T)$ is the bulk free energy per spin and $F^\times(h, h_1, T)$ the surface free energy per surface spin.[7]

Since, in general, $F^\times$ is nonanalytic at the bulk critical temperature[1] T_c, we introduce[1,2] the new exponents $\alpha^\times$ for the surface specific heat, $C^\times(T)$; $\gamma^\times$ for the surface susceptibility[8] $\chi^\times(T) = -\partial^2 F^\times/\partial h^2$; β_1 for the surface magnetization $M_1(T) = -\partial F^\times/\partial h_1$; γ_1 for the layer susceptibility $\chi_1(T) = -\partial^2 F^\times/\partial h_1 \partial h$; $\gamma_{1,1}$ for the local susceptibility $\chi_{1,1}(T) = -\partial^2 F^\times/\partial h_1^2$, etc.[9] In this paper we discuss the relation of these "surface" exponents to each other and to the standard bulk exponents,[10] on the basis of a generalized homogeneity assumption[11] for the singular part, F_s, of $F(n, h, h_1, T)$.

Explicitly, we assume that in the critical region, we may write

$$F_s(n, h, h_1, T) \approx Q(n, h, h_1, \dot{t}) \quad (2)$$

as $n\to\infty$ and $h, h_1, \dot{t}\to 0$, where the function Q satisfies the homogeneity relation

$$Q(ln, l^{-\phi} h, l^{-\phi_1} h_1, l^{-\theta}\dot{t}) = l^{\psi} Q(n, h, h_1, \dot{t}) , \quad (3)$$

where we introduce the new exponent ϕ_1 to scale h_1. The *shifted* temperature deviation $\dot{t}$ is defined by

$$\dot{t} = [T - T_c(n)]/T_c = t + \epsilon(n) , \quad (4)$$

where $T_c(n)$ is the finite-size critical temperature,[12] $T_c = T_c(\infty)$ is the corresponding bulk critical temperature, $t = (T - T_c)/T_c$, and the fractional shift

$$\epsilon(n) = [T_c - T_c(n)]/T_c \approx b/n^\lambda \quad \text{as } n\to\infty , \quad (5)$$

with λ the shift exponent.[1]

If we choose $l = 1/n$ in (3), we may combine (2) and (3) into the single scaling postulate

$$F_s(n, h, h_1, T) \approx n^{\psi} Q(1, n^{\phi} h, n^{\phi_1} h_1, n^{\theta}\dot{t}) \quad (6)$$

as $n\to\infty$ and $h, h_1, \dot{t}\to 0$, which identifies θ, ϕ, and ϕ_1 as crossover exponents[11] in terms of n. In zero field ($h = h_1 = 0$) the specific heat $C(n, T)$ and total susceptibility per spin $\chi(n, T)$ may be written

$$Y(n, T) \approx n^{\omega} X(n^{\theta}\dot{t}), \quad n\to\infty, \quad \dot{t}\to 0 , \quad (7)$$

where $\omega = \psi + 2\theta$ or $\psi + 2\phi$ if $Y = C$ or χ, respectively, and the scaling functions $X(x)$ are given by appropriate derivatives of Q. This result is of precisely the form discussed by Fisher and Barber,[1] where θ is the *rounding exponent*.[1] Hence from their arguments we find

$$\theta = 1/\nu, \quad \psi = (\alpha - 2)/\nu,$$
$$\phi = -\tfrac{1}{2}(\psi - \theta\gamma) = \Delta/\nu, \tag{8}$$

where $\alpha, \beta, \gamma, \nu$, and Δ are standard bulk exponents.[10,13] A more detailed investigation[1] of the behavior of $X(x)$ for large x yields the predictions

$$\alpha^{\times} = \alpha + \nu, \quad \gamma^{\times} = \gamma + \nu \quad \text{if } \lambda > 1, \tag{9}$$

$$\alpha^{\times} = \alpha + 1, \quad \gamma^{\times} = \gamma + 1 \quad \text{if } \lambda = 1 \text{ and } \nu < 1. \tag{10}$$

Turning now to the behavior of the derivatives of F with respect to h_1 we find that in zero field, $\chi_1(n, T)$ and $\chi_{1,1}(n, T)$ are also of the form (7) with $\omega = \psi + \phi_1 + \phi$ and $\psi + 2\phi_1$, respectively. The analysis of Ref. 1 is again applicable, except to note that as $n \to \infty$, we now require $Y(n, T)$ to approach $Y_1(T)/n$. Hence the exponents γ_1 and $\gamma_{1,1}$ must satisfy

$$\psi + \phi_1 + \phi - \gamma_1\theta = \psi + 2\phi_1 - \gamma_{1,1}\theta = -1, \tag{11}$$

which yields

$$\phi_1 = \frac{2 - \alpha + \gamma_1 - \Delta}{\nu} - 1 = \frac{\Delta - \gamma_1 + \gamma_{1,1}}{\nu}$$
$$= \frac{2 - \alpha + \gamma_{1,1}}{2\nu} - \frac{1}{2}. \tag{12}$$

Combining (11) with (8) yields the first of our new exponent relations:

$$2\gamma_1 - \gamma_{1,1} = \gamma + \nu. \tag{13}$$

The behavior of the surface magnetization $M_1(T)$ also follows by a similar argument[14] and we obtain the second relation

$$\beta_1 + \gamma_1 = \beta + \gamma. \tag{14}$$

Eliminating γ_1 between (13) and (14) gives

$$2\beta_1 + \gamma_{1,1} = 2\beta + \gamma - \nu = 2 - (\alpha + \nu). \tag{15}$$

If the shift exponent λ exceeds unity, we may combine this result with (9) to obtain

$$\alpha^{\times} + 2\beta_1 + \gamma_{1,1} = 2, \tag{16}$$

which was first proposed by Binder and Hohenberg.[2] Note, however, that this last result does *not* follow if $\lambda = 1$ and $\nu < 1$.

The actual surface scaling theory of Binder and Hohenberg[2] may also be deduced from the basic homogeneity postulate (3). To do so we choose $l = |\dot{t}|^{\nu}$ in (3), which yields, in place of (6), the alternative scaling form

$$F_s(n, h, h_1, T) \approx |\dot{t}|^{2-\alpha} Q(n|\dot{t}|^{\nu}, h/|\dot{t}|^{\Delta}, h_1/|\dot{t}|^{\phi\Delta_1}, 1) \tag{17}$$

as $n \to \infty$ and $|\dot{t}|$, h, $h_1 \to 0$, where $\Delta_1 = \varphi_1\mu$. If we now assume that

$$Q(x, y, z, 1) \approx Q_{\infty}(y) + x^{-1} Q^{\times}(y, z) + \cdots, \tag{18}$$

as $x \to \infty$ at fixed y and z, and compare with (1) we obtain a scaled form for $F^{\times}$;

$$F^{\times}(h, h_1, T) \approx \tfrac{1}{2}|t|^{2-\alpha^{\times}} Q^{\times}(h/|t|^{\Delta}, h_1/|t|^{\Delta_1}), \tag{19}$$

provided $\lambda > 1$. With $h = 0$, this is precisely of the form proposed by Binder and Hohenberg.[2] If $\lambda = 1$, there is an additional contribution to $F^{\times}$ from the first term in (18) and we find

$$F^{\times}(h, h_1, T) \approx \tfrac{1}{2}|t|^{2-(\alpha+\nu)} Q^{\times}(h/|t|^{\Delta}, h_1/|t|^{\Delta_1})$$
$$+ \tfrac{1}{2} b |t|^{2-\alpha^{\times}}[(2-\alpha)Q_{\infty}(h/|t|^{\Delta}) - \Delta(h/|t|^{\Delta})Q_{\infty}'(h/|t|^{\Delta})], \tag{20}$$

where b is the amplitude of the shift (5) and the prime denotes differentiation. Hence the single homogeneity assumption (3) yields *both* the finite-size scaling of Fisher[1] and the surface scaling of Hohenberg,[2] and thus unifies these two apparently distinct scaling formulations for surface problems.

The question now arises to the validity of the new exponent relations (13)–(15)[15] for actual model or real systems. The existing published[1-3] values and estimates of surface exponents for d-dimensional Ising models ($d = 2, 3$) are summarized in Table I. The exact values[3] of β_1 and $\gamma_{1,1}$ for the two-dimensional Ising model ($\alpha = 0$, $\beta = \frac{1}{8}$, $\gamma = \frac{7}{4}$, $\nu = 1$) satisfy (15), while either (13) or (14) then gives $\gamma_1 = \frac{11}{8}$ in agreement with the numerical estimate.[2] The predictions (13)–(15) are also satisfied by the mean-field results[2] $\beta_1 = 1$, $\gamma_1 = \frac{1}{2}$, $\gamma_{1,1} = -\frac{1}{2}$, while (13) is also in accord with exact calculations on the spherical model,[16] in all dimensions, which yield[17] $\gamma_1 = -\gamma_{1,1} = 1/(d-2)$ for $2 < d < 4$. From (12) we explicitly find that $\phi_1 = 1$ for mean-field theory and $\phi_1 = \frac{1}{2}$ for the $d = 2$ Ising model and $d = 3$ spherical model.

On the other hand, for the three-dimensional Ising model ($\gamma \simeq \frac{5}{4}$, $\beta \simeq \frac{5}{16}$, $\nu \simeq 0.64$) the situation is less definite. The estimates[2] of γ_1 and $\gamma_{1,1}$ satisfy (13) only within the relatively large error bars quoted. With these values we may conclude from (13) that $\phi_1 \simeq 1.0 \pm 0.15$, while (14) and (16) predict $\beta_1 \simeq 0.68 \pm 0.08$. However, a preliminary analysis of a direct low-temperature expansion[18] for $M_1(T)$ indicates $\beta_1 \simeq 1.0 \pm 0.12$. While this result must be considered as somewhat tentative (the series is relatively short), the validity of the general homogeneity postulate remains open to question for the $d = 3$ Ising model.

With regard to real systems, the only experimentally measured surface exponent to date is $\beta_1 \simeq 1$ for nickel oxide (NiO) by low-energy-electron diffraction (LEED).[4] Although this does agree with the tentative estimate quoted above for the $d = 3$ Ising model, a definite comparison is premature on both theoretical and experimental grounds.

In summary, the exponent relations (13)–(15) appear to be in agreement with the known exponents for several model systems, but uncertain on existing estimates for the $d = 3$ Ising model and possibly real sys-

TABLE I. Surface exponents for Ising models.

Dimension d	Shift Λ	Magnetization β_1	Specific heat $\alpha^\times$	Susceptibilities $\gamma^\times$	γ_1	$\gamma_{1,1}$
2	1^a	$\frac{1}{2}^b$	1^b	$\frac{11}{4}\pm 0.05^c$	$\frac{11}{8}\pm 0.05^c$	$0\ (\log)^b$
3	1.56 ± 0.15^d	$?^e$	?	1.95 ± 0.08^d	$\frac{7}{8}\pm 0.08^c$	$0\sim\frac{1}{8}{}^c$

[a]Exact calculation (Ref. 1).
[b]Exact calculation (Ref. 3).
[c]Series estimate (Ref. 2).
[d]Series estimate (Ref. 1).
[e]No direct estimate yet available.

tems. Undoubtedly, more theoretical and experimental study is required before our understanding of the critical behavior of surface properties approaches that of bulk critical phenomena.

Note added in proof. Fisher (private communication) has pointed out that the exponent Δ_1 appearing in (17) is conceivably model independent. For the $d=2$ Ising model, mean-field theory and the spherical model (all d) it has the value $\frac{1}{2}$. If we assume for the $d=3$ Ising model that $\Delta_1\simeq 0.5$, we find from (12) and (14), $\gamma_1\simeq 0.82$, $\gamma_{1,1}\simeq -0.2$, $\beta_1\simeq 0.73$. This estimate for γ_1 is in good agreement with the numerical estimate (Table I), while the existing series for $\chi_{1,1}$ and M_1 must be viewed as too short to exclude the estimates for $\gamma_{1,1}$ and β_1.

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[1]M. E., Fisher, in *Proceedings of the 1970 Enrico Fermi Summer School, Course No. 51* (Academic, New York, 1972), and references cited therein; see also, M. E. Fisher and M. N. Barber, Phys. Rev. Lett. **28**, 1516 (1972).

[2]K. Binder and P. C. Hohenberg, Phys. Rev. B **6**, 3461 (1972), and references cited therein.

[3]B. M. McCoy and T. T. Wu, Phys. Rev. **162**, 436 (1967). Some of the results of this work were obtained independently by M. E. Fisher and A. E. Ferdinand [Phys. Rev. Lett. **19**, 169 (1967)].

[4]T. Wolfram, R. E. De Wames, W. F. Hall, and P. W. Palmberg, Surf. Sci. **28**, 45 (1971).

[5]For simplicity we consider a hypercubic lattice, but definitions are readily extended to other lattices and, in fact, to continuum systems.

[6]That is, h_1 couples only to spins in the surface layers.

[7]Recalling that the system has *two* free surfaces.

[8]In this and subsequent definitions, the fields h and h_1 are understood to be put equal to zero after differentiation.

[9]Other exponents of interest are $\delta_{1,1}$ describing the local critical isotherm $M_1(h_1)$ and local gap exponents; see Ref. 2. One should also, in principle, distinguish low- and high-temperature exponents $\gamma^{\times\prime}$, γ_1', etc; in the absence of any evidence at all on this point we assume $\gamma^{\times\prime}=\gamma^\times$. (See also Ref. 14.)

[10]See, e.g., M. E. Fisher, Rep. Prog. Phys. **30**, 615 (1967).

[11]See, e.g., M. E. Fisher and D. M. Jasnow, *Theory of Correlations in the Critical Region* (Academic, New York, to be published). A similar idea has been introduced by A. Hankey and H. E. Stanley [Phys. Rev. B **6**, 3515 (1972)], although these authors make the additional assumption of "extended scaling," which replaces $\dot{t}$ by t.

[12]Or more generally, in case there is no sharp transition for finite n, a pseudocritical temperature; see Ref. 1 and M. N. Barber and M. E. Fisher, Ann. Phys. (N. Y.) (to be published).

[13]$\Delta=\beta+\gamma=\beta\delta$ is the gap exponent; see Ref.10.

[14]Since β_1 is defined for $T<T_c$, we require the scaling function for $M_1(T,n)$ to behave as $|x|^{\beta_1}$, as $x\to-\infty$. Unless $\omega'\neq\omega$ there can, however, be no distinction between γ_1' and γ_1, etc. The possibility of $\omega'\neq\omega$ may be excluded by considering the behavior at T_c of say $M=-\partial F/\partial h$ as a function of h.

[15]The validity of the relations (9) and (10) for $\alpha^\times$ and $\gamma^\times$ has been discussed by Fisher and Barber (Ref.1).

[16]G. S. Joyce, in *Phase Transitions and Critical Phenomena* (Academic, New York, 1962), Vol. 2, p. 375. For this model $\gamma=2(d=3)$, $1(d\geq 4)$, and $\nu=\gamma/2$.

[17]M. N. Barber (unpublished). Additional logarithmic factors occur for $d=4$, but do not change the conclusion.

[18]M. N. Barber (unpublished).