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Phase Transitions and Static Spin Correlations in Ising Models with Free Surfaces

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Phase transitions in Ising models with free surfaces are studied from various points of view, including a phenomenological Landau theory, high-temperature series expansions, and a scaling theory for thermodynamic quantities and correlation functions. In the presence of a surface a number of new critical exponents must be defined. These arise because of the existence of "surface" terms in the thermodynamic functions, and because of the anisotropy of space and lack of translational symmetry introduced by the surface. The need for these new critical exponents already appears in the phenomenological theory, which is discussed in detail and related to the microscopic mean-field approximation. The essential new parameter appearing in this theory is an extrapolation length λ which enters the boundary condition on the magnetization at the surface. For magnetic systems this length is of the order of the interaction range, in contrast to superconductors, where it is usually much larger. In order to go beyond the mean-field theory, high-temperature series expansions are carried out for the Ising half-space, to tenth order in two dimensions and to eighth order in three dimensions. A scaling theory is developed both for thermodynamic functions and for spin correlations near the surface, and relations are found among the exponents of the half-space. Both the scaling theory and the numerical calculations are compared with the exact solution of the Ising half-plane (two dimensions) by McCoy and Wu, and agreement is found wherever the theory is applicable. In analogy to the bulk situation, the scaling theory is found to agree with mean-field theory in four dimensions. The prediction of the present work which is most easily accessible to experiment is the temperature dependence of the magnetization at the surface, with critical exponent estimated to be $\beta_1 = 2/3$. The mean-field result, $\beta_1 = 1$, seems to agree more closely with presently available experiment, and more work is needed to clarify the situation.

I. INTRODUCTION

Phase transitions in magnetic systems have been studied extensively both theoretically and experimentally in recent years.[1-3] Although experiments are carried out on finite systems with real surfaces, the theoretical models used for calculations have nearly always been infinite in extent. The usual justification for neglecting surface effects is that these only involve a fraction of order $N^{(d-1)/d}$ of the total number of atoms N, and this fraction is vanishingly small for large N (d is the dimensionality of the system). In addition, most real crystal surfaces are quite imperfect, and thus difficult to characterize in terms of simple models. Nevertheless, if high accuracy is desired, it seems important to study the influence of surfaces on magnetic properties in more detail, particularly near the phase-transition point, where spin correlations have very large range. Moreover, as techniques of sample preparation and measurements become more refined, it seems likely that the specific properties of magnetic surfaces themselves will receive greater experimental attention. The aim of the present paper is to study the effects of surfaces on magnetic phase transitions by a careful analysis of a simple model: the Ising half-space.

Apart from early work on the transition temperature of magnetic films,[4] there seems to have been little theoretical work on magnetic surface phenomena near T_c until quite recently.[5] The most complete picture is provided by the phenomenological "Ginzburg-Landau" theory,[6] which is a direct generalization of the Landau theory of second-order phase transitions[7] to systems with surfaces. This theory was discussed very recently from a purely phenomenological point of view by Kaganov and Omelyanchouk,[8] and microscopically by Mills[9] and by Wolfram *et al.*[9a] Of course, the quantitative predictions of the phenomenological theory are not expected to be accurate for surfaces any more than they are for the bulk, and more reliable theories are desirable. For two dimensions the exact solution by McCoy and Wu[10] of the Ising half-plane with nearest-neighbor interactions[11] provides an essentially complete generalization of Onsager's[12] work in the bulk, and it demonstrates concretely that the phenomenological theory has only qualitative validity. For three-dimensional systems a great deal of information has been obtained in the bulk from high-temperature series expansions[1] and from phenomenological scaling theories[13] which provide relations between critical exponents. In this paper we generalize this work to systems with surfaces, and attempt to elucidate the relationship between the various phenomenological theories and microscopic calculations, both exact[10,11,14] and approximate.[9,9a] Previous applications of scaling theories and high-temperature-expansion methods to magnetic systems with surfaces have been carried out by Watson,[15] Fisher and his co-workers,[14,16,17] and Wolfram *et al.*[9a]; our work is a continuation of those efforts.

In the presence of a surface it is necessary to define a number of new critical exponents, and we have determined some of these for the semi-infinite Ising model from high-temperature series expansions. The remaining exponents were obtained from "scaling relations" analogous to the ones which have been discussed extensively in bulk systems.[13] The new scaling laws were also shown to hold exactly in two dimensions. For three dimensions, we estimate that our determination of the new exponents is accurate to better than ±0.1 so that the deviations from the mean-field values can be considered to be significant.

The main physical effect of the surface is twofold: first, a "thermodynamic" effect, whereby the free energy of the system has a term proportional to the number of surface atoms, in addition to the bulk contribution proportional to the total number of atoms. The "surface free energy" leads to the introduction of "surface" exponents, such as α_s, describing the divergence of the surface specific heat. The second effect of the surface is geometrical, and has to do with the breaking of translational invariance and isotropy (which holds asymptotically in the bulk as $T \to T_c$). The thermodynamic average of a local operator will be different near the surface from its value deep in the bulk, and correlation functions involving spins at the surface are also expected to be strongly modified. These changes are described by the values of "local" exponents, e.g., the exponent β_1 for the magnetization at the surface. The above distinction between surface exponents and local exponents is not the whole story, however, since there are, for instance, at least two different "local" susceptibilities at the surface: The first is the response χ_1 of a surface spin to a uniform field acting throughout the system, and the second is the response $\chi_{1,1}$ to a field acting only on the surface. The need for making these distinctions (which already exist in the molecular-field theory) will become apparent in what follows.

An even more important distinction must be made between a surface quantity, e.g., the surface free energy discussed above and the "interface free energy" for a bulk system.[11,15] This latter quantity only exists in the ordered state; it is defined analogously to the surface free energy, but in a situation in which the magnetization is lined up in one direction at one end of the sample and in the opposite direction at the other end. The interface free energy per unit area is the "interface tension," which is unfortunately traditionally called "surface tension!"

From an experimental point of view the most interesting quantities are the surface magnetization m_1 and the correlation function for spins on the surface, since these can be probed by low-energy electron diffraction (LEED),[18,19,9a] or possibly by Mössbauer measurements. In the molecular-field theory the surface magnetization is given by the equation[8,9,9a]

$$m_1 = m_b \lambda / \xi , \qquad (1.1)$$

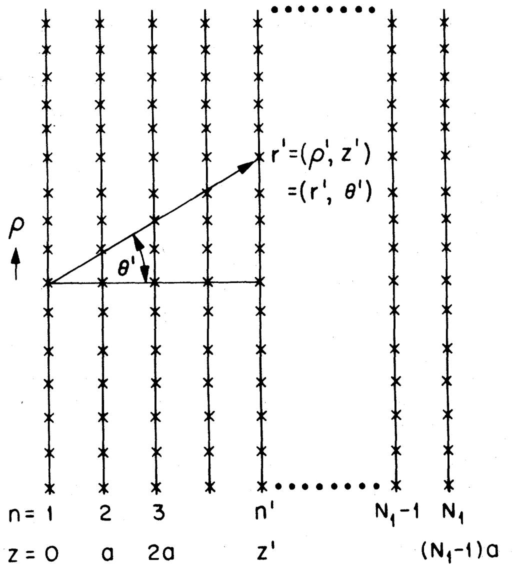

FIG. 1. d-dimensional Ising film of N_1 layers shown schematically in cross section. Each vertical line represents a $(d-1)$-dimensional layer, with coordinate $\vec{\rho}$. The layers are indexed by n, which goes from 1 to N_1, or by z, going from 0 to $(N_1-1)a$. An arbitrary point is denoted by the vector $\vec{r}\,'$, or the pair $(\vec{\rho}\,', z')$. For many purposes it is sufficient to give the two numbers $r' \equiv |\vec{r}\,'|$ and θ', the angle with the normal to the surface. For $N_1 \to \infty$ the system is a half-space with a free surface at $z=0$.

where m_b is the bulk magnetization,[20] ξ is the correlation length, and λ is an "extrapolation length" which completely characterizes the effect of the surface. If λ is constant near T_c, then Eq. (1.1) implies that $m_1 \propto (T_c - T)$, or in terms of the critical exponent β_1 for m_1, that $\beta_1 = \beta + \nu$.[9a] As we discuss below, however, this result of molecular-field theory is not expected to hold generally. In two dimensions the exact answer is $\beta_1 = \frac{1}{2}$ and in three dimensions our scaling analysis yields $\beta_1 \approx \frac{2}{3}$. Thus the concept of an extrapolation length λ seems to have no validity outside of mean-field theory. The result of the phenomenological theory concerning spin correlations in the surface is more nearly correct: The mean-field calculation yields a finite cusp for $\chi_{1,1}$ and we find a weak singularity $(0 \lesssim \gamma_{1,1} \lesssim \frac{1}{8})$ in three dimensions (for $d=2$, $\chi_{1,1}$ has a logarithmic divergence). The weakness of the singularity is not due to a finite correlation range, however, but to a large exponent η in the surface, even in molecular-field theory. This point was misinterpreted somewhat by Mills,[9] although his calculation is correct.

From the above discussion it is clear that accurate measurements of the surface magnetization and local response $\chi_{1,1}$ would be of great interest, since one can make concrete predictions concerning their critical behavior.

In Sec. II the phenomenological theory of magnetic systems with surfaces is reviewed, first from the general Ginzburg–Landau point of view, and then using the molecular-field approximation. With the additional length parameter λ mentioned above, all the thermodynamic quantities and spin-correlation functions can be calculated, for films and semi-infinite systems. The parameter λ can in general be either positive or negative and its calculation in terms of microscopic quantities is possible only in simple cases. Generally speaking, for spin systems λ is shown to be of the order of the interaction range, in contrast to superconductors, where λ is much larger than any other length in the system (see Sec. II B4). In Sec. III precise definitions are presented of the new exponents which arise near a surface. Section IV discusses the various exact theories for magnetic systems with free surfaces. In particular, a review is given of the results of McCoy and Wu[10] on the Ising half-plane with nearest-neighbor interactions. In addition, an exact reformulation is described, in which the d-dimensional half-space is separated into the bulk system, plus a $(d-1)$-dimensional surface system, with a complicated temperature-dependent interaction. In Sec. V a scaling theory is postulated for this surface system which yields relations between the exponents of the half-space. This scaling is shown to hold exactly in two dimensions, and to be completely consistent with molecular-field theory in four dimensions. Section V also contains a discussion of the scaling of correlations near the surface and of Fisher's theory of scaling in finite systems.[16] In Sec. VI the high-temperature series for the Ising half-space in two and three dimensions are presented (to tenth order for $d=2$ and to eighth order for $d=3$). The resulting exponents are calculated and shown to be consistent with exact results and scaling theories, where applicable. All of the remaining exponents are then determined by using the previously derived scaling relations. The exponent values are given in Tables II and VII. Section VII summarizes the main results of the present work.

Let us note, finally, that although we consider only Ising models explicitly in this paper many of our results also apply more generally, e.g., to superfluid helium.[21]

II. MEAN-FIELD THEORY

A. Generalized Landau Theory

Let us consider a d-dimensional spin system consisting of N_1 "layers," each one of which is an infinite $(d-1)$-dimensional system (see Fig. 1). We shall assume for concreteness a simple-cubic lattice with spacing a. The layers are indexed by

n, which goes from 1 to N_1. When N_1 goes to infinity the first layer is a free surface in a semi-infinite system. Let the coordinates of a lattice site be denoted by $(\vec{\rho}, z)$, where $z=(n-1)a$ and $\vec{\rho}$ is a $(d-1)$-dimensional vector within each layer; we shall often denote the pair $(\vec{\rho}, z)$ by the vector $\vec{r}$, and the spin at $\vec{r}$ by $\sigma_{\vec{\rho},z}=\sigma_{\vec{\rho},n}=\sigma_{\vec{r}}$.

For an infinite system the Landau theory[7] is characterized by a free energy

$$F=\int d\vec{r}\{Am^2(\vec{r})+Bm^4(\vec{r})+C[\nabla_{\vec{r}}\, m(\vec{r})]^2\}\ , \tag{2.1}$$

where

$$m(\vec{r})=\langle\sigma_{\vec{r}}\rangle\ , \tag{2.2}$$

$$A=\alpha(T-T_{c0})/T_{c0}\equiv\alpha t\ , \tag{2.3}$$

and α, B, C, and T_{c0} are constants.

For a finite slab of length

$$L_1=aN_1\ , \tag{2.4}$$

the generalization of Eq. (2.1) is[8]

$$F=\int d\vec{\rho}\int_0^{L_1}dz\,\{Am^2(\vec{r})+Bm^4(\vec{r})+C[\nabla_{\vec{r}}\, m(\vec{r})]^2\}+F_1\ , \tag{2.5}$$

where the surface contribution F_1 is expanded in even powers of the *local* magnetization, and only the first term is retained, i.e.,

$$F_1=C\lambda^{-1}\int d\vec{\rho}\,[m^2(\vec{\rho}, z=0)+m^2(\vec{\rho}, z=L_1)]\ . \tag{2.6}$$

Equation (2.6) introduces a new phenomenological parameter λ, with dimensions of length. We show in Eqs. (2.8) and (2.9) below that Eq. (2.6) is equivalent to a boundary condition on $m(z)$. For many purposes it is possible to neglect variations within the layers and to replace $m(\vec{r})$ by its average over $\vec{\rho}$, which we shall denote simply by $m(z)$. Then Eq. (2.5) becomes

$$F\propto\int_0^{L_1}dz\left[Am^2(z)+Bm^4(z)+C\left(\frac{\partial m}{\partial z}\right)^2\right]+C\lambda^{-1}[m^2(z=0)+m^2(z=L_1)]\ . \tag{2.7}$$

The parameter λ is not specified for the moment, and in fact even its sign is not determined *a priori*. The spatial distribution of magnetization may be obtained by solving the Ginzburg–Landau equation[6]

$$\xi_0^{-2}t\,m(z)+bm^3(z)-\frac{\partial^2 m}{\partial z^2}=0\ , \tag{2.8}$$

with the associated boundary conditions

$$\frac{\partial m}{\partial z}-\lambda^{-1}m=0\ , \quad z=0 \tag{2.9a}$$

$$\frac{\partial m}{\partial z}+\lambda^{-1}m=0\ , \quad z=L_1\ . \tag{2.9b}$$

Equations (2.8) and (2.9) are obtained by functional differentiation of Eq. (2.7); we may introduce the correlation length for $t>0$:

$$\xi\equiv\xi_0 t^{-1/2}=(C/\alpha)^{1/2}t^{-1/2}\ , \quad t>0 \tag{2.10}$$

and the constant

$$b\equiv 2B/C\ . \tag{2.11}$$

The spin-spin correlation function

$$C(\vec{r}, \vec{r}\,')\equiv\langle\sigma_{\vec{r}}\sigma_{\vec{r}\,'}\rangle \tag{2.12}$$

is the solution of the linear differential equation[9]

$$-\nabla_{\vec{r}}^2\, C(\vec{r}, \vec{r}\,')+\xi^{-2}C(\vec{r}, \vec{r}\,')=a\delta(\vec{r}-\vec{r}\,')\ , \tag{2.13}$$

with the boundary condition

$$\frac{\partial}{\partial z}C(\vec{r}, \vec{r}\,')=\lambda^{-1}C(\vec{r}, \vec{r}\,')\ , \quad z=0 \tag{2.14}$$

and a similar boundary condition at $z'=0$. The above equation is valid for $T\gtrsim T_c$ in the semi-infinite system. The boundary conditions on the other variables are the usual ones—that the correlations should go to zero at infinity (for $T>T_c$).

The phenomenological theory with the one new parameter λ leads to many interesting consequences,[8,9] of which we shall list the most significant.

1. Magnetization at the Surface

In the semi-infinite system the value $m_1\equiv m(z=0)$ of the magnetization in the first layer may be obtained quite simply from Eq. (2.8), by multiplying by $m'=\partial m/\partial z$, integrating with respect to z from 0 to ∞, and using the boundary condition at $z=0$ [Eq. (2.9a)]. This yields

$$\tfrac{1}{2}\xi^{-2}(m_\infty^2-m_1^2)+\tfrac{1}{4}b(m_\infty^4-m_1^4)+\tfrac{1}{2}\lambda^{-2}m_1^2=0\ . \tag{2.15}$$

For positive surface energy ($\lambda>0$) we have

$$m_\infty^2=m_b^2=(-t)(\xi_0^2 b)^{-1}\ ,$$

and we obtain, for $t<0$,

$$m_1=\lambda(2b)^{-1/2}\xi_0^{-2}(-t)=(\lambda/\xi)\,m_b\ , \quad t\to 0^- \tag{2.16}$$

where for $t<0$

$$\xi^{-2}\equiv(\alpha/2c)(-t)=\tfrac{1}{2}\xi_0^{-2}(-t)\ , \qquad t<0\ . \tag{2.17}$$

For negative surface energy ($\lambda<0$), we have $m_\infty=0$ for $T>T_{c0}$ $(t>0)$, and a magnetization at the surface first appears at a reduced temperature

$$t_c=(\xi_0/\lambda)^2\ . \tag{2.18}$$

The behavior of m_1 in the temperature interval $0<t<t_c$, i.e., $T_c<T<T_c(1+t_c)$, may also be simply obtained from Eq. (2.15), putting $m_\infty=0$. We find

$$m_1=(2/b\,\xi_0^2)(t_c-t)^{1/2}\ , \quad t\to t_c^-\ . \tag{2.19}$$

As $t\to 0^+$ $(T\to T_c^+)$, m_1 tends to $(2t_c/b\,\xi_0^2)^{1/2}$ and the bulk of the material becomes ordered. It is interesting to note the difference in critical exponent for the surface and bulk magnetizations for $\lambda > 0$, namely, $m_b \propto (-t)^{1/2}$ and $m_1 \propto (-t)$. For $\lambda < 0$, on the other hand, we have $m_1 \propto (t_c - t)^{1/2}$.

2. T_c *Shift for a Film*

For a film of finite thickness L_1, Eqs. (2.8) and (2.9) may be linearized and solved to find the shift in transition temperature, $t_c = (T_c - T_{c0})/T_{c0}$, where T_{c0} is the bulk transition temperature [Eq. (2.3)]. We quote here the results of Refs. 8 and 9a (in our notation, e.g., $L_1 = 2d$): For $\lambda > 0$, the transition temperature is lowered:

$$t_c(L_1) = -(2\xi_0^2/L_1\lambda), \quad L_1 \ll \lambda \tag{2.20}$$

$$t_c(L_1) = -(\pi^2\xi_0^2/L_1^2), \quad L_1 \gg \lambda . \tag{2.21}$$

For $\lambda < 0$, the transition temperature is raised:

$$t_c(L_1) = 2|\lambda|\xi_0^2/L_1, \quad L_1 \ll |\lambda| \tag{2.22}$$

$$t_c(L_1) = (\xi_0^2/\lambda^2), \qquad L_1 \gg |\lambda| . \tag{2.23}$$

The result in Eq. (2.23), which is independent of L_1, was already obtained for $L_1 \to \infty$ in Eq. (2.18). It is interesting to note that for $\lambda > 0$ and large L_1 we have

$$t_c(L_1) \propto L_1^{-2} \sim L_1^{-1/\nu} , \tag{2.24}$$

where $\nu = \frac{1}{2}$ is the exponent of the correlation length. This scaling result, which follows from a correct molecular-field theory, was first obtained for the analogous case of superfluids by Ginzburg and Pitaevskii,[21] and for magnetic systems by Brodkorb and co-workers.[4] We shall discuss Eq. (2.24) further in Secs. II B 3 and V below.

3. *Surface Specific Heat*

Let us calculate the specific heat of our system for $\lambda > 0$. The free energy per unit area in the layer for $t < 0$ is given by

$$F = C\int_0^{L_1}[t\,\xi_0^{-2}m^2(z) + \tfrac{1}{2}bm^4(z)]\,dz + C\lambda^{-1}[m^2(0) + m^2(L_1)] . \tag{2.25}$$

Since from the solution of Eq. (2.28) $m(z)$ only differs from its bulk value $m_b = (-t/\xi_0^2 b)^{1/2}$ over a region of length ξ from the surface, we can easily show that

$$F \approx L_1(\tfrac{1}{2}tC\xi_0^{-2}m_b^2) - 2Cm_1^2\xi/3\lambda^2 = L_1F_B - (2C/3\xi^3 b) , \tag{2.26}$$

where $F_B = \frac{1}{2}Ct\,\xi_0^{-2}m_b^2$ is the bulk free energy per unit volume (more precisely, the free-energy difference between the disordered and the ordered states). For the total system with volume $\mathcal{V}$, the free energy is

$$F_{\text{tot}} = \mathcal{V}(F_B + 2L_1^{-1}F_s) , \tag{2.27}$$

where the surface free energy is

$$F_s = -[C(-t)^{3/2}/3\xi_0^3 b] . \tag{2.28}$$

Note that F_s is not equal to F_1 in Eq. (2.5).

Differentiating F_s twice with respect to T we find the surface specific heat

$$C_s = (C/4\,\xi_0^3\,bT_c)(-t)^{-1/2} , \tag{2.29}$$

which diverges as $t \to 0^-$ with an exponent

$$\alpha_s = \tfrac{1}{2} . \tag{2.30}$$

4. *Correlation Function*

For positive λ, Eqs. (2.13) and (2.14) for the correlation function in the semi-infinite system were solved by Mills.[9] The result is, in our notation,

$$C(\vec{q}, z, z') = [a/2\gamma(\vec{q})](1 - \Gamma e^{-2\gamma(\vec{q})z'})\,e^{-\gamma(\vec{q})(z-z')} , \qquad z > z' \tag{2.31}$$

$$C(\vec{q}, z, z') = [a/2\gamma(\vec{q})](e^{\gamma(\vec{q})(z-z')} - \Gamma e^{-\gamma(\vec{q})(z+z')}) , \qquad 0 < z < z' \tag{2.32}$$

where

$$\begin{gathered}\gamma(\vec{q}) = \xi_0^{-1}(t + q^2\xi_0^2)^{1/2} , \\ \Gamma = \Gamma(\vec{q}) = [1 - \lambda\gamma(\vec{q})]/[1 + \lambda\gamma(\vec{q})] ,\end{gathered} \tag{2.33}$$

and $C(\vec{q}, z, z')$ is the Fourier transform of $C(\vec{r}, \vec{r}\,')$ with respect to the $(d-1)$-dimensional coordinate difference $\vec{\rho} - \vec{\rho}\,'$ in the layers:

$$C(\vec{r}, \vec{r}\,') = \int \frac{d\vec{q}}{(2\pi)^{d-1}}\, C(\vec{q}, z, z')\, e^{i\vec{q}\cdot(\vec{\rho}-\vec{\rho}\,')} . \tag{2.34}$$

For z and z' deep in the bulk, i.e., for $z, z' \gg \xi$, it was shown by Mills[9] that $C(\vec{q}, z, z')$ depends on $z - z'$ and may be Fourier transformed with respect to this variable. If $\vec{q}_\perp$ is the corresponding wave vector we obtain the usual Ornstein–Zernike form[20]:

$$C_b(Q) = a\xi^{-2}(1 + Q^2\xi^2)^{-1} , \tag{2.35}$$

where

$$Q^2 = q_\perp^2 + q^2 .$$

For $z' = 0$ we have, from Eq. (2.31),

$$C_1(\vec{q}, z) \equiv C(\vec{q}, z, z' = 0) = [a/2\gamma(\vec{q})]\,e^{-\gamma(\vec{q})z}(1 - \Gamma) . \tag{2.36}$$

Let us calculate its Fourier transform:

$$C_1(\bar{\rho}, z) = \int \frac{d\vec{q}}{(2\pi)^{d-1}}\, e^{i\vec{q}\cdot(\vec{\rho}-\vec{\rho}\,')}\, C_1(\vec{q}, z) , \tag{2.37}$$

with $\bar{\rho} \equiv |\vec{\rho} - \vec{\rho}\,'|$. Since Eq. (2.36) for $C_1(\vec{q}, z)$ is only valid for small $\vec{q}$, we must integrate Eq. (2.37) to some upper cutoff $q_c \approx \xi_0^{-1}$.

We shall calculate $C(\tilde{\rho}, z)$ for correlations parallel and perpendicular to the surface, respectively,

$$C_{\parallel}(\tilde{\rho}) \equiv C_1(\tilde{\rho}, z=0) = \int \frac{d\vec{q}}{(2\pi)^{d-1}}\, e^{i\vec{q}\cdot(\vec{\rho}-\vec{\rho}\,')} \times (a\lambda)[1+\lambda\gamma(\vec{q})]^{-1} . \qquad (2.38)$$

For simplicity, we shall evaluate the integral for a one-dimensional surface, i.e., $d=2$, since in the phenomenological theory the dimensionality should not affect the critical exponents (we must, however, drop the normalization factor a in front of the correlation function):

$$C_{\parallel}(\tilde{\rho}) = (\lambda/\pi)\int_0^{q_c} dq \cos q\tilde{\rho}\,[1+(\lambda/\xi_0)(t+q^2\xi_0^2)^{1/2}]^{-1} . \qquad (2.39)$$

We are interested in the contributions to this integral coming from $q \ll \xi_0^{-1} \approx q_c$, so we may expand the denominator. The first term only has contributions near $q=q_c$ and is not of interest,[22] and the next term may be integrated by parts to yield

$$C_{\parallel}(\tilde{\rho}) \sim (\lambda^2 t/\xi_0^2\pi)\int_0^{\infty} dx\, \cos x\,[(t\tilde{\rho}^2/\xi_0^2)+x^2]^{-3/2} , \qquad (2.40)$$

where the upper limit of the integral $x_c = q_c\tilde{\rho}$ has been set to infinity for $\tilde{\rho} \gg \xi_0 \sim q_c^{-1}$. The integral in Eq. (2.40) is a Bessel function[23] and we find

$$C_{\parallel}(\tilde{\rho}) = (\lambda^2/\pi)(\xi\tilde{\rho})^{-1}K_1(\tilde{\rho}/\xi) , \qquad (2.41)$$

which has the limiting behavior

$$C_{\parallel}(\tilde{\rho}) \sim \lambda^2/\pi\tilde{\rho}^2 , \qquad \tilde{\rho} \ll \xi \qquad (2.42a)$$

$$C_{\parallel}(\tilde{\rho}) \sim [\lambda^2/(2\pi\xi\tilde{\rho}^3)^{1/2}]\, e^{-\tilde{\rho}/\xi} , \qquad \tilde{\rho} \gg \xi . \qquad (2.42b)$$

From Eq. (2.42) it is clear that the *range* of correlations is the bulk correlation length ξ. At T_c, however, the parallel correlations die out as $\tilde{\rho}^{-2}$, rather than being logarithmic, as they would be in a bulk two-dimensional system. In terms of the usual exponent η we have for parallel correlations

$$C_{\parallel}(\tilde{\rho}) \propto r^{2-d-\eta_{\parallel}}, \quad \eta_{\parallel} = 2 , \quad t=0 . \qquad (2.43)$$

Because of the rapid falloff of the correlations at T_c, the parallel susceptibility $\chi_{1,1}$, which is proportional to $C_1(q=0, z=0)$, remains finite at T_c (see below) even though the range of correlations is infinite. As mentioned in the Introduction, this point was missed by Mills [see discussion after Eq. (28) of Ref. 9], who attributed the finiteness of the susceptibility to a finite correlation range.

Let us calculate the perpendicular correlation function, namely,

$$C_{\perp}(z) = C_1(\tilde{\rho}=0, z) = \int \frac{d\vec{q}}{(2\pi)^{d-1}}\, C_1(\vec{q}, z) . \qquad (2.44)$$

Using Eq. (2.36) we see that for large z and small t the integral is entirely dominated by small q and we may replace the term $[1+\lambda\gamma(\vec{q})]^{-1}$ by unity, since $\gamma(\vec{q}) \to 0$. The integral is then straightforward and we find, for $d=3$,

$$C_{\perp}(z) = (\lambda a/2\pi z^2)(1+z/\xi)\, e^{-z/\xi} \qquad (2.45)$$

and, for $d=2$,

$$C_{\perp}(z) = (\lambda/\pi z) , \qquad z \ll \xi \qquad (2.46a)$$

$$C_{\perp}(z) = [\lambda/(2\pi z\xi)^{1/2}]\, e^{-z/\xi} , \qquad z \gg \xi . \qquad (2.46b)$$

In terms of the exponent $\eta_{\perp}$, defined by

$$C_{\perp}(z) = z^{2-d-\eta_{\perp}} f(z/\xi) , \qquad (2.47)$$

we find here

$$\eta_{\perp} = 1 \qquad (2.48)$$

for both $d=2$ and $d=3$.

As stated above, the susceptibility in the surface, namely the response of a surface spin to a field acting only in the surface, remains finite at T_c. In fact, it has a cusp, as can be seen from Eq. (2.36):

$$\chi_{1,1} \propto C_{\parallel}(\vec{q}=0) = C_1(\vec{q}=0,\ z=z'=0) \sim \frac{a\lambda}{1+\lambda\xi^{-1}} . \qquad (2.49)$$

On the other hand, the response of a surface spin to a uniform field is divergent. Indeed, let us denote this response by χ_1; we have

$$\chi_1 \sim \int d\vec{\rho} \int_0^{\infty} dz'\, C(\vec{\rho}, z') = \int_0^{\infty} dz'\, C(q=0, z') \sim (a\lambda)\xi \propto t^{-1/2} , \qquad (2.50)$$

where we have used Eq. (2.45) for $d=3$. If in analogy with the bulk exponent γ we introduce exponents $\gamma_{1,1}$ and γ_1,

$$\chi_{1,1} = \chi_{1,1}^0\, t^{-\gamma_{1,1}} , \quad t \to 0 \qquad (2.51)$$

$$\chi_1 = \chi_1^0\, t^{-\gamma_1} , \quad t \to 0 \qquad (2.52)$$

then we see that according to Eqs. (2.49) and (2.50) we have

$$\gamma_{1,1} = -\tfrac{1}{2} \text{ (finite cusp)} , \qquad (2.53)$$

$$\gamma_1 = \tfrac{1}{2} , \qquad (2.54)$$

whereas, of course, in the phenomenological theory $\gamma = 1$. As discussed in Sec. III A below we may also define a surface susceptibility in analogy with the surface specific heat, Eq. (2.29). In the present case its exponent turns out to be

$$\gamma_s = \tfrac{3}{2} . \qquad (2.54a)$$

B. Molecular-Field Approximation

The preceding discussion was entirely phenomenological, and was based on the usual parameters of the bulk Landau theory (ξ_0, T_{c0}, and b, say), plus the additional parameter λ. Since this parameter determines the surface behavior completely, it is natural to attempt to estimate its magnitude. In particular, we may try to use the molecular-field approximation to calculate λ from the starting Hamiltonian, just as one can calculate the parameters of the bulk Landau theory in simple cases.[24]

A general formula for λ has been given by de Gennes,[25] in the context of the Ginzburg–Landau theory of superconductivity. Let $J(\vec{r}', \vec{r}'')$ be the exchange interaction acting between spins at $\vec{r}'$ and $\vec{r}''$. Then in the molecular-field theory the transition temperature is given by the largest eigenvalue T_c of the linear equation[24,25]

$$m(\vec{r}) = \frac{(k_B T)^{-1}}{a^d} \int d\vec{r}'\, J(\vec{r}, \vec{r}')\, m(\vec{r}') , \tag{2.55}$$

where $a^{-d} \int d\vec{r}'$ denotes a sum over all the spins in the half-space. (Only for long-range potentials can the sum be replaced by an integral, but we shall use the integral notation in the general case.) Let us suppose in general that the interaction is modified by the surface over a finite distance δ, i.e., that

$$J(\vec{r}, \vec{r}') = J_0(|\vec{r} - \vec{r}'|) \quad \text{for } z, z' > \delta . \tag{2.56}$$

The function J_0 is the interaction in the bulk, which we suppose has a range R defined by

$$R^2 = \frac{\int d\vec{r}\, r^2 J_0(r)}{\int d\vec{r}\, J_0(r)} . \tag{2.57}$$

Note that the length δ must be at least as large as R. In terms of J_0, the bulk transition temperature is given by

$$(k_B T_c)^{-1} = a^{-d} \int d\vec{r}\, J_0(r) = \sum_{\vec{r}} J_0(r) . \tag{2.58}$$

We may define the length λ by requiring the function $m(z)$ to be of the form[25]

$$m(z) = m_1(1 + \lambda/z) \quad \text{for } \delta \leqslant z < \xi . \tag{2.59a}$$

Far from the surface, i.e., for $z \gg \xi$, we have

$$m(z) = m_b , \quad z \gg \xi . \tag{2.59b}$$

Clearly at T_c this latter region is absent, since $\xi \to \infty$. A formal expression for λ has been derived by de Gennes (Ref. 25, p. 230); in our notation it is

$$\lambda^{-1} = (m_1 k_B T_c A R^2 a^d / 2d)^{-1} \times \int d\vec{r}\, d\vec{r}'\, [J_0(\vec{r} - \vec{r}') - J(\vec{r}, \vec{r}')]\, m(\vec{r}') , \tag{2.60}$$

where A is the area (volume) of the $(d-1)$-dimensional surface and the $\vec{r}$ integral is over all space, including $z < 0$ [note that $J(\vec{r}, \vec{r}') = 0$ for $z < 0$]. This general expression is of course only a rewriting of the integral equation (2.55), since it involves the unknown solution $m(\vec{r}')$. It is a convenient expression, however, since the integral only contributes within a finite layer (of thickness δ) of the surface because of Eq. (2.56). This expression for λ^{-1} is analogous to the formula for the phase shift and scattering length in a scattering problem, using effective-range theory.[26] If the exchange interaction is modified by the surface over infinite distances, as it probably is in an itinerant-electron system,[27] then the extrapolation length λ is probably not a useful concept. It is clear from Eq. (2.60) that if the interaction is sufficiently large at the surface compared to its bulk value, then λ will be negative, and the surface region will order before the bulk, as is to be expected intuitively. However, even in the present molecular-field approximation one cannot, in general, derive the condition for the appearance of ordering in the surface (i.e., for $\lambda^{-1} \leqslant 0$), since Eq. (2.60) for λ depends on the unknown function $m(\vec{r}')$. For the simple case of nearest-neighbor interactions this condition was found by Mills,[9] as we discuss in Sec. II B 2 below. We have also analyzed this problem using high-temperature series expansions, and shall report our results elsewhere.[28]

In order to elucidate the microscopic significance of the length λ we shall discuss a number of simple cases.

1. Interaction Unmodified by Surface

The simplest case to consider is

$$J(\vec{r}, \vec{r}') = J_0(\vec{r} - \vec{r}') , \quad z, z' \geqslant 0 \tag{2.61a}$$

$$J(\vec{r}, \vec{r}') = 0 , \qquad z \text{ or } z' < 0 \tag{2.61b}$$

i.e., when the only effect of the surface is to create "missing bonds." Then let

$$F(z') \equiv (k_B T_C)^{-1} \int \frac{d\vec{r}}{a^d}\, J(\vec{r}, \vec{r}') \equiv (k_B T_C)^{-1} \int \frac{d\vec{r}}{a^d}\, J_0(|\vec{r} - \vec{r}'|) , \quad z > 0 . \tag{2.62}$$

If J_0 has a range R [Eq. (2.57)], then $F(z')$ is a function of the form

$$F(z') = 1 , \qquad z' \geqslant cR \tag{2.63a}$$

$$F(z') = \tfrac{1}{2}(1 + z'/cR) , \quad 0 \leqslant z' \leqslant cR \tag{2.63b}$$

where c is a constant of order unity. Now Eq. (2.60) may be integrated with respect to $\vec{r}$ and with respect to the component $\vec{\rho}'$ of $\vec{r}'$, parallel to the surface, yielding

$$\lambda^{-1} = (2d/R^2 m_1) \int_0^\infty dz'\, [1 - F(z')]\, m(z') , \tag{2.64a}$$

$$\lambda^{-1} = (d/R^2 m_1) \int_0^{cR} dz'\, (1 - z'/cR)\, m(z') . \tag{2.64b}$$

Equation (2.61) implies that the length δ [Eq. (2.56)] is of order R. Choosing $\delta = cR$, we may rearrange

Eq. (2.64) to read

$$R/(\lambda + cR) = cd \int_0^1 dx\,(1-x)\,f(x)\ , \tag{2.65}$$

where

$$f(z'/R) \equiv m(z')/m(R)\ . \tag{2.66}$$

The function f is positive and goes from a value $f(0)$ lying between 0 and 1 to $f(1)=1$. Therefore, the right-hand side of Eq. (2.65) is a positive number of order unity, and it follows that λ is of order R, i.e.,

$$\lambda = \bar{c}R\ , \tag{2.67}$$

with $\bar{c} > 0$ of order unity. Thus an interaction with range R leads to an extrapolation length λ which is also of order R.

2. Nearest-Neighbor Interactions

For nearest-neighbor interactions Eq. (2.64) may be calculated completely by carrying out the sums over $\vec{r}$ and $\vec{r}'$ in Eq. (2.60), remembering that $a^{-1}\int dz = \sum_z$. The function $F(z')$ of Eq. (2.62) has the values

$$F(0) = (\zeta - 1)/\zeta\ , \tag{2.68a}$$

$$F(z') = 1\ , \quad z' \geq a \tag{2.68b}$$

where ζ is the number of neighbors. Then Eq. (2.64a) only has a contribution at $z'=0$, and the unknown constant $m_1 = m(z'=0)$ drops out. The result is

$$\lambda^{-1} = (2da/R^2\zeta) = a^{-1}\ , \tag{2.69}$$

since $R=a$ and $\zeta = 2d$ in a simple-cubic lattice. This result was derived directly from Eq. (2.55) by Mills.[9] Moreover, it is easy to see that if the coupling in the surface layer is $J(1+\Delta)$ Eq. (2.64a) implies

$$\lambda = a/(1-4\Delta)\ , \tag{2.70}$$

which is also Mills's[9] result [Eq. (6b)]. Thus for nearest-neighbor interactions in a simple-cubic lattice the extrapolation length λ is just equal to the lattice spacing a (for $\Delta = 0$), and the condition for the appearance of surface ordering is $\lambda^{-1}=0$, i.e.,

$$\Delta_c = \tfrac{1}{4}\ . \tag{2.71}$$

A more exact calculation, using high-temperature series, yields[28]

$$\Delta_c \approx 0.6 \tag{2.72}$$

for this case.

3. One-Dimensional Case

For certain simple potentials in one-dimensional systems the integral equation (2.55) can be solved completely, and the length λ obtained from the solution. These potentials must of course be of long range ($R \gg a$), so that Eq. (2.55) can indeed be considered an integral equation. We shall treat two cases.

(i) $J(z,z') = J\,e^{-|z-z'|\sqrt{2}/R}$.

We assume that $J(z,z')=0$ for z or $z'<0$. The integral equation for $m(z)$ [Eq. (2.55)] may be solved exactly by Wiener–Hopf techniques.[29] The smallest eigenvalue, $(k_B T_c)^{-1}$ (corresponding to the largest temperature), is

$$k_B T_c = \sqrt{2}\,JR/a \tag{2.73}$$

and the corresponding solution is[29]

$$m(z) = m_1(1 + z\sqrt{2}/R)\ , \tag{2.74}$$

which retains the linear form up to the surface. By comparing Eq. (2.58) with Eq. (2.74) we find

$$\lambda = R/\sqrt{2}\ . \tag{2.75}$$

For a film of thickness $L_1 \gg R$, we may find the smallest eigenvalue of Eq. (2.55), whose eigenfunction has zero slope at $z = \frac{1}{2}L_1$. From the complete set of eigenfunctions[29] it is readily seen that

$$m(z) = \cos(|t_c|^{1/2} z\sqrt{2}/R) + \frac{\sin(|t_c|^{1/2} z\sqrt{2}/R)}{|t_c|^{1/2}}\ , \tag{2.76}$$

where

$$t_c(L_1) = -(\pi^2R^2/2L_1^2) = -\pi^2\xi_0^2/L_1^2\ , \tag{2.77}$$

which agrees with Eq. (2.21). Thus the effect of the finite boundaries is not only to change the interactions (i.e., the number of neighbors seen by the spins near the surface), but also to distort the eigenfunctions. If only the first effect is taken into account, the shift in transition temperature is proportional to the fraction of missing neighbors, which is of order R/L_1. This is the answer referred to by Fisher[30] as the "naive mean-field picture." In fact, however, the eigenfunction is also modified by the surface, and there is a much smaller shift, of order $(R/L_1)^2$. This scaling result [cf. Eq. (2.24)] is a direct consequence of the existence of an extrapolation length λ, and it follows directly from the molecular-field Ornstein–Zernike theory.[8,9a]

$$\text{(ii)}\quad J(z,z') = J\{\cosh[\pi(z-z')/R]\}^{-1}\ . \tag{2.78}$$

This interaction also leads to an exactly soluble integral equation in one dimension.[31] The solution at T_c can be shown to be[31]

$$m(z) = m_1 e^{\pi z/2R} P_{-1/2}(e^{\pi z/R})\ , \tag{2.79}$$

which has the asymptotic behavior

$$m(z) = m_1[1 + (\pi/32)^{1/2}(z/R)^{1/2} + \cdots]\ , \quad z \ll R \tag{2.80a}$$

and

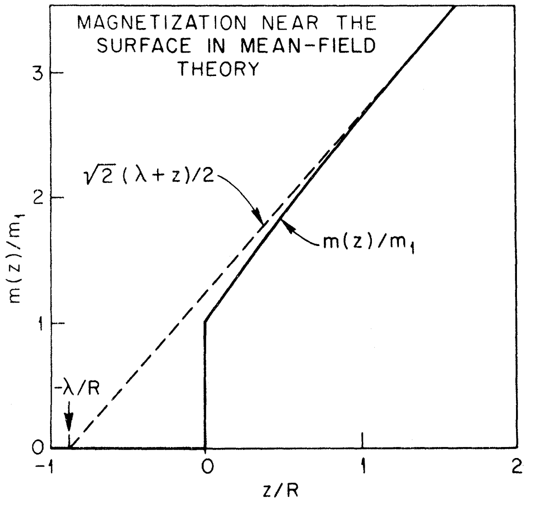

FIG. 2. Magnetization of T_c as a function of position, according to the molecular-field theory in a one-dimensional system with interaction given by Eq. (2.78). The behavior is linear at large z, with an extrapolation length $\lambda=(4\ln 2/\pi)R$, but there is a deviation from linear behavior at small z.

$$m(z)=m_1[(32)^{1/2}\ln 2/\pi](1+\pi z/4R\ln 2)\ ,\quad z\gg R\ . \tag{2.80b}$$

Thus for this potential the extrapolation length is given by

$$\lambda=(4\ln 2/\pi)R\ . \tag{2.81}$$

The eigenfunction is not a straight line in this case, as can be seen from the plot in Fig. 2.

4. *Case of Superconductors*

The BCS theory of superconductivity[25] is, of course, a molecular-field theory, but the kernel of Eq. (2.55) is not a simple function of the form considered above. The range of $J_0(|\vec{r}-\vec{r}\,'|)$, defined in Eq. (2.57), is the BCS coherence length ξ_0, which is much larger than the interelectron distance $a\sim k_F^{-1}$. On the other hand, the function $F(z')$ of Eq. (2.62) (which describes the range over which the surface influences the kernel) differs from unity only over a short distance, of order a. The length λ is basically the ratio of the second moment of J_0 (i.e., ξ_0^2) to the distance over which the surface modifies the zeroth moment, namely,

$$\lambda\sim\xi_0^2/a\gg\xi_0\ . \tag{2.82}$$

For a spin system, on the other hand, both the range R of J_0 and the range of influence δ of the surface are typically of the same order, so that λ is also of order R or ξ_0. It is the electronic nature of the superconductor which leads to the very large extrapolation length in Eq. (2.82). In that case there is essentially no shift in transition temperature[6] for a film of finite thickness L_1, since $\lambda>\xi$, even though $L_1\lesssim\xi_0$. Of course, very near T_c the length ξ becomes infinite, and we will have a very small shift in T_c given by Eq. (2.20), namely,

$$\Delta T_c/T_c=-(\xi_0^2/L_1\lambda)\sim-(L_1k_F)^{-1}\ . \tag{2.83}$$

Such an effect has been discussed for superconductors by Naugle, Glover, and Moormann,[32] both theoretically and experimentally.

III. PRECISE DEFINITIONS OF EXPONENTS

In Sec. II we have seen that critical behavior is severely modified in the presence of a surface, even in the molecular-field approximation. In order to study the effect of a surface more exactly it is necessary to define a certain number of new critical exponents, some of which have already been considered.

A. Thermodynamic Quantities

Consider the system discussed in Sec. II A, consisting of N_1 layers, each of which is a $(d-1)$-dimensional system of $N^*=N/N_1$ particles. For large N the total free energy of the system F_N has the form

$$\lim_{N\to\infty}F_N(T,H)=NF_b(T,H)+2N^*F_s(T,H)+\cdots\ . \tag{3.1}$$

Equation (3.1) defines the surface free energy F_s, for which the usual critical exponents may be considered. For example, the surface specific heat

$$C_{s,H}=-T\left(\frac{\partial^2F_s}{\partial T^2}\right)_H \tag{3.2}$$

has the exponent α_s:

$$C_s\sim C_s^0\,t^{-\alpha_s}\ . \tag{3.3}$$

Similarly, there is a surface susceptibility χ_s with exponent γ_s:

$$\chi_s\sim\chi_s^0\,t^{-\gamma_s}\ . \tag{3.4}$$

These exponents were denoted $\alpha^{\times}$ and $\gamma^{\times}$ by Fisher.[16]

In addition to these surface quantities, which are defined in terms of the asymptotic behavior of the total free energy or total susceptibility for large N, one can define "local" quantities by considering averages of local operators. For example, the magnetization in the nth layer is

$$m_n=\langle\sigma_{\vec{\rho},n}\rangle\ . \tag{3.5}$$

Clearly, this expression is independent of the coordinate $\vec{\rho}$, and it defines an exponent β_n:

$$m_n\sim m_n^0\,t^{\beta_n}\ ,\quad t\to0^+\ . \tag{3.6}$$

We may now define local susceptibilities as the responses of m_n to different magnetic fields. If we first consider a field H which acts *uniformly* throughout the whole system then we have

$$\chi_n = \left(\frac{\partial m_n}{\partial H} \right)_T , \qquad (3.7)$$

with exponent γ_n:

$$\chi_n \sim \chi_n^0 \, t^{-\gamma_n} , \quad t \to 0^+ . \qquad (3.8)$$

If, however, we apply a field H_n only to the spins on the nth layer, then we have a different local susceptibility,

$$\chi_{n,n} = \left(\frac{\partial m_n}{\partial H_n} \right)_T , \qquad (3.9a)$$

$$\chi_{n,n} \sim \chi_{n,n}^0 \, t^{-\gamma_{n,n}} , \quad t \to 0^+ . \qquad (3.9b)$$

In terms of the correlation function [Eq. (2.12)], we have

$$\chi_n = (k_B T)^{-1} \sum_{n', \vec{\rho}\,'} C(\vec{\rho}, n; \vec{\rho}\,', n') \qquad (3.10)$$

and

$$\chi_{n,n} = (k_B T)^{-1} \sum_{\vec{\rho}\,'} C(\vec{\rho}, n; \vec{\rho}\,', n) . \qquad (3.11)$$

It is also easy to show that

$$\chi_s = \lim_{N_1 \to \infty} \frac{1}{N_1} \sum_{n=1}^{N_1} (\chi_b - \chi_n) . \qquad (3.12)$$

Interface Free Energy

As mentioned in the Introduction, it is important to distinguish the surface free energy from the interface free energy, which is defined for a bulk system and calculated[11,15] by taking a ladder of N_1 horizontal bonds, say, which have a reversed sign of the interaction $-J$. Then the total free energy for $N \to \infty$ can be written

$$\lim_{N \to \infty} F_N = N F_b + N_1 F_{\text{int}} , \qquad (3.13)$$

$$F_{\text{int}} = a^{(d-1)} \sigma_{\text{int}} , \qquad (3.14)$$

where F_{int} is the interface free energy and σ_{int} is the interface tension (misleadingly called surface tension). In general F_{int} and F_s are different (see Sec. IV A).

B. Correlation Exponents

Let us consider the correlation function $C(\vec{r}\,' = 0; \vec{\rho}, z)$ between a spin at the surface ($\vec{\rho}\,' = 0$, $z' = 0$) and an arbitrary spin at a distance $\vec{\rho}, z$. In contrast to the case of an infinite medium, this correlation function will depend sensitively on the orientation of the vector $(\vec{\rho}, z)$ even near T_c. Let us denote the magnitude of this vector by r and its angle with the normal to the surface by θ ($\theta = \frac{1}{2}\pi$ for $z = 0$, $\theta = 0$ for $\vec{\rho} = 0$) and write

$$C_1(\vec{\rho}, z) = C_1(r, \theta) \equiv C(\vec{\rho}\,' = 0,\ z' = 0 ; \vec{\rho}, z) . \qquad (3.15)$$

For fixed $T > T_c$ we define the *true* correlation range ξ_θ by the relation

$$C_1(r, \theta) \underset{r \to \infty}{\sim} f(r, \theta) \, e^{-r/\xi_\theta(t)} , \quad t > 0 \qquad (3.16)$$

where $f(r, \theta)$ decays more slowly than an exponential. Interesting special cases of Eq. (3.16) are the cases of parallel correlations ($\theta = \frac{1}{2}\pi$),

$$\xi_{\pi/2}(t) \equiv \xi_\parallel(t) \sim \xi_\parallel^0 \, t^{-\nu_\parallel} , \quad t \to 0^+ \qquad (3.17)$$

and perpendicular correlations ($\theta = 0$),

$$\xi_0(t) \equiv \xi_\perp(t) \sim \xi_\perp^0 \, t^{-\nu_\perp} , \quad t \to 0^+ . \qquad (3.18)$$

In addition to the true correlation range we may define *effective* correlation ranges in terms of moments of the correlation function. These are the quantities which can be easily evaluated from series expansions; they are

$$\bar{\xi}_\perp^2 \equiv \tfrac{1}{2} \chi_1^{-1} \sum_{\vec{\rho}, z} z^2 C_1(\vec{\rho}, z) \sim (\bar{\xi}_\perp^0)^2 |t|^{-2\bar{\nu}_\perp} , \qquad (3.19)$$

$$\bar{\xi}_\parallel^2 \equiv \frac{1}{2(d-1)} \chi_1^{-1} \sum_{\vec{\rho}, z} \rho^2 C_1(\vec{\rho}, z) \sim (\bar{\xi}_\parallel^0)^2 |t|^{-2\bar{\nu}_\parallel} , \qquad (3.20)$$

$$\bar{\xi}^2 \equiv d^{-1} [\bar{\xi}_\perp^2 + (d-1) \bar{\xi}_\parallel^2] \sim (\bar{\xi}^0)^2 |t|^{-2\bar{\nu}} . \qquad (3.21)$$

For the bulk correlation function on a cubic lattice it can be shown (see Ref. 46 below) that the true and effective correlation ranges are asymptotically equal as $T \to T_c$.

For $T = T_c$ the correlations decay according to a power

$$C_1(r, \theta) \underset{r \to \infty}{\sim} \frac{A(\theta)}{r^{d-2+\eta_\theta}} , \quad t = 0 \qquad (3.22)$$

which again leads to the special cases $\eta_\perp$ and $\eta_\parallel$. We note that throughout this discussion of the correlation function we have held one spin fixed at the surface ($n = 1$) and have suppressed the index 1 on all exponents, which should be there for completeness in analogy to Eq. (3.8) or Eq. (3.10). The necessity for introducing this large number of new critical exponents should be apparent already from the phenomenological theory considered in Sec. II.

IV. EXACT RESULTS

A. Ising Half-Plane

The most interesting exact results concerning surface effects are contained in the remarkable paper of McCoy and Wu[10] (hereafter referred to as MW) on the Ising half-plane with nearest-neighbor interactions. These authors succeeded in solving the problem exactly in the presence of a field H_1 acting on the surface spins alone. They thus calculated many of the critical exponents[11] defined in Sec. III and, moreover, found the correlation function $C_\parallel$ for arbitrary separations between the spins on the surface and arbitrary values of the temperature and magnetic field H_1. Since their paper involves extremely complicated calculations, it is sometimes difficult to recognize the important physical results. We shall therefore summarize these and transcribe them into our notation. We specialize their results to equal interactions among all spins and to the vicinity of the critical point (which is the same as in the bulk system).

1. Thermodynamic Quantities

The boundary magnetization m_1 has been evaluated as a function of $t \equiv (T-T_c)/T_c$ and $h_1 \equiv H_1/k_B T_c$. The results are [cf. MW, (5.29) and (5.30)] for $t<0$

$$m_1 = c^{1/2}\bar{c}^{1/2}(-t)^{1/2}\operatorname{sgn} h_1 - 2\pi^{-1} c h_1 \ln(-\bar{c}t + h_1^2) \tag{4.1}$$

and for $t>0$

$$m_1 = -2\pi^{-1} c h_1 \ln(\bar{c}t + h_1^2), \tag{4.2}$$

where[33]

$$c \equiv e^{4J/k_B T_c} = 1+\sqrt{2}, \tag{4.3}$$

$$\bar{c} \equiv 8J/k_B T_c = 2\ln(1+\sqrt{2}). \tag{4.4}$$

[Note that there is a misprint in MW (5.29); the second term on the right-hand side should contain $|z_2|^{-1}$ and not $|z_2|^{-2}$, as can be seen from MW (5.26).] It follows from Eqs. (4.1) and (4.2) that the zero-field susceptibility is

$$\chi_{1,1} \equiv \left(\frac{\partial m_1}{\partial h_1}\right)_t = -2\pi^{-1} c \ln|t|. \tag{4.5}$$

The surface free energy has also been calculated, and the surface specific heat is given by[10,11] [MW (4.45)]

$$C_s = (4\pi)^{-1}\bar{c}(-t)^{-1}. \tag{4.6}$$

As pointed out by MW, this specific heat comes from an entropy which diverges at T_c, unlike the bulk entropy. Moreover, the specific heat C_s is negative above T_c, and there exists a "latent heat" [MW (4.46)] whose physical significance is obscure. It is interesting to contrast the surface free energy leading to Eq. (4.6) with the interface free energy [Eq. (3.13)], which for the two-dimensional case has the values[11]

$$F_i = 0, \quad t>0 \tag{4.7}$$

$$F_i \propto -t, \quad t<0. \tag{4.8}$$

From Eqs. (4.7) and (4.8) it is clear that the interface specific heat does not diverge at T_c. Let us write down the critical exponents which follow from the above results:

$$\beta_1 = \tfrac{1}{2}, \tag{4.9}$$

$$\gamma_{1,1} = 0 \text{ (logarithm)}, \tag{4.10}$$

$$\delta_{1,1} = 1, \tag{4.11}$$

$$\alpha_s = 1. \tag{4.12}$$

In addition, MW have calculated the magnetization in interior rows. In particular they find for the second row (MW, Sec. IX)

$$\beta_2 = \tfrac{1}{2}, \tag{4.13}$$

and they conjecture that $\beta_n = \frac{1}{2}$ for all finite n. Since for the bulk we have $\beta = \frac{1}{8}$,[1] it is clear that the range of temperature over which m_n follows the exponent β_n must go to zero as n grows large.

It is interesting to compare the exact result $\beta_1 = \frac{1}{2}$ with that derived in Sec. II using the concept of a temperature-independent extrapolation length λ. From Eq. (2.16) we have

$$m_1 = (\lambda/\xi) m_b, \tag{4.14}$$

which implies

$$\beta_1 = \beta + \nu. \tag{4.15}$$

Since for two dimensions $\beta = \frac{1}{8}$ and $\nu = 1$, we would have $\beta_1 = \frac{9}{8}$, which is even larger than the molecular-field answer $\beta_1 = 1$ [Eq. (2.16)], and completely different from the exact result. We conclude that the surface magnetization is not in general determined by a temperature-independent boundary condition.

2. Parallel Correlations

The parallel correlation function $C_{\parallel}(\rho, t, h_1)$ has been calculated exactly. Let us write down the explicit answer for interesting limiting cases, taking the lattice spacing a to be unity.

a. $h_1 = 0$, $\rho \to \infty$, *t fixed*. In this case we have [MW (8.41) and (8.52)]

$$C_{\parallel}(\rho, t, 0) \sim m_1^2 + (2\pi)^{-1/2} c\, \xi_{\parallel}^{1/2} \rho^{-3/2} e^{-\rho/\xi_{\parallel}} \tag{4.16}$$

for both $t>0$ and $t<0$, where, of course, $m_1 = 0$ for $t>0$ and where

$$\xi_{\parallel} \equiv (\bar{c})^{-1}|t|^{-1} = \xi_{\parallel}^0 |t|^{-\nu_{\parallel}} \tag{4.17}$$

is the parallel correlation length. Note that both $\xi_{\parallel}$ and the coefficient which occurs in front of the exponential are entirely symmetric for $t>0$ and $t<0$. This is in contrast to the situation in the bulk two-dimensional case,[34,35] but entirely consistent with the results of Fisher and Camp[36] (see Sec. IV C).

b. $h_1 = 0$, $\rho \to \infty$, $t \to 0$, $\rho/\xi_{\parallel}$ *fixed*. In this case we have [MW (8.87) and (8.88)]

$$C_{\parallel}(\rho, t, 0) = m_1^2 + \pi^{-1} c \rho^{-1} \left[F(\rho/\xi_{\parallel}) - \frac{1}{2\rho}\left(\frac{\rho}{\xi_{\parallel}}\right)^2 K_1(\rho/\xi_{\parallel}) + O(\rho^{-2}) \right], \tag{4.18}$$

again for $t>0$ and $t<0$, where

$$F(x) \equiv x \int_x^\infty dy\, y^{-1} K_1(y) , \qquad (4.19)$$

$K_1(y)$ being a modified Bessel function. The function $F(x)$ has the limiting values

$$F(x) \sim (\pi/2)^{1/2} x^{-1/2} e^{-x} , \quad x \gg 1 \qquad (4.20a)$$

$$F(x) \sim 1 - \tfrac{1}{2} x^2 \ln x , \qquad x \ll 1 . \qquad (4.20b)$$

Therefore Eq. (4.18) goes precisely into Eq. (4.16) when $\rho \gg \xi_{\parallel}$. This suggests that the correlation function satisfies strong scaling[37] in this case, as it supposedly does in the bulk.[37,38]

c. $t=0$, $\rho \to \infty$, h_1 *fixed.* From MW (8.81) we have

$$C_{\parallel}(\rho, 0, h_1) = m_1^2 + (4\pi^2 c^2 h_1^6 \rho^4)^{-1} , \qquad (4.21)$$

where we have used MW (8.92). It is interesting to note that for $t=0$ the correlations decay according to a power law for fixed h_1 at large ρ, in contrast to the situation for $h_1 = 0$ and fixed t.

d. $t=0$, $h_1 \to 0$, $\rho \to \infty$, $h_1 \rho^2$ *fixed.* In this case, according to MW (8.90)–(8.97), we have

$$C_{\parallel}(\rho, 0, h_1) = m_1^2 + 4\pi^{-2} c^2 \rho^{-1} G(\rho h_1^2), \qquad (4.22)$$

where

$$G(x) = g(x) - 4c^2 x\, g^2(x) - x \left(\frac{dg}{dx}\right)^2 , \qquad (4.23)$$

$$g(x) = \int_0^\infty dy\, e^{-yx} (y^2 + 4c^2)^{-1} . \qquad (4.24)$$

[Note that $g(x)$ is incorrectly given in MW (8.97), where the factor of 4 is missing from the denominator. The correct form follows from MW (8.96).] The function $G(x)$ has the following limiting forms:

$$G(x) \sim \pi / 4c , \qquad x \ll 1 \qquad (4.25a)$$

$$G(x) \sim (16 x^3 c^4)^{-1} , \quad x \gg 1 . \qquad (4.25b)$$

From Eq. (4.25b) we see that for $\rho h_1^2 \gg 1$ Eq. (4.22) just reduces to Eq. (4.21), which holds for fixed h_1 as $\rho \to \infty$.

This result suggests once again that strong scaling[37] holds at T_c as a function of h_1, where the correlation length is

$$\xi(h_1) = h_1^{-2} . \qquad (4.26)$$

Since the correction terms are not given explicitly, we can also not assert that strong scaling has been proved rigorously in this case.

It follows from Eqs. (4.17) and (4.18) that the critical exponents are

$$\nu_{\parallel} = 1 = \nu_b , \qquad (4.27)$$

$$\eta_{\parallel} = 1 \neq \eta_b , \qquad (4.28)$$

and the exponent $\mu_{\parallel}$ of $\xi(h_1)$ [Eq. (4.26)] is

$$\mu_{\parallel} = 2 = \nu_{\parallel} / \beta_1 \delta_{1,1} . \qquad (4.29)$$

Moreover, it can be verified that the values of $\xi_{\parallel}^0$ are the same as those of ξ^0 for the bulk above T_c.[34,35]

This completes our presentation of the results of MW. We shall discuss some implications of these results in Sec. V. The perpendicular correlations were not calculated by MW, and they are clearly more difficult to obtain. It seems feasible, however, to find $C_{\perp}(z)$ at T_c, which would be an interesting result, since it would yield $\eta_{\perp}$. In Sec. VI B we shall derive a scaling estimate for this exponent.

B. Reduction to a Pure Surface Problem

In this section we shall derive an exact transformation of the d-dimensional half-space into a problem involving only the $(d-1)$-dimensional surface, plus the bulk problem. It will turn out that the interaction between the spins in the surface will be very much more complicated than the simple Ising interaction of our starting system, but certain exact statements can be made about this Hamiltonian. Let the starting interaction be written in the form

$$\mathcal{H} \equiv -J \sum_{i=1}^{N} \sigma_i \sigma_{i+\hat\delta} - H_1 \sum_{\alpha=1}^{N^*} \sigma_{\alpha,1} , \qquad (4.30)$$

where $i = (\alpha, n)$ is a general lattice site in the system, in the nth layer ($n = 1, \ldots, N_1$), and α labels the position within each $(d-1)$-dimensional layer containing $N^* = N/N_1$ sites. The vector $\hat\delta$ is a nearest-neighbor distance, and the field H_1 acts only on the first layer ($n=1$). The partition function

$$Z_N = 2^{-N} \sum_{\{\sigma_i = \pm 1\}} e^{-\mathcal{H}/k_B T} \qquad (4.31)$$

may be separated into a sum over the σ_i in the first layer, $\sigma_{\alpha,1}$, and a sum over all the other $\sigma_i = \sigma_{\beta,n}$ with $n \geq 2$. In Appendix A we show that the total free energy

$$F_N = (k_B T) \ln Z_N \qquad (4.32)$$

may be written in the following form:

$$F_N = N F_b(T) + N^* F^*(T, H_1) , \qquad (4.33)$$

where

$$F^*(T, H_1) = (k_B T) 2^{-N^*} \sum_{\{\sigma_\alpha^* = \pm 1\}} e^{-\mathcal{H}^*/k_B T} , \qquad (4.34)$$

$$\mathcal{H}^* = -J \sum_{\alpha=1}^{N^*} \sigma_\alpha^* \sigma_{\alpha+\hat\delta^*}^* - H_1 \sum_{\alpha=1}^{N^*} \sigma_\alpha^* + N^* V^*(T, \{\sigma_\alpha^*\}) , \qquad (4.35)$$

and $\sigma_\alpha^* = \sigma_{\alpha,1}$ is confined to the surface ($n=1$), with $\hat\delta^*$ a nearest-neighbor distance in the surface. The Hamiltonian $\mathcal{H}^*$ contains a very complicated interaction energy $V^*(T, \{\sigma_\alpha^*\})$, which is defined in Eqs. (A5) and (A6) and can be shown to remain finite

TABLE I. Correspondence between surface system and half-space.

Surface system	Half-space	$d=2$	Mean field $d=4$
α^*	α_s	1	$\frac{1}{2}$
β^*	β_1	$\frac{1}{2}$	1
γ^*	$\gamma_{1,1}$	0	$-\frac{1}{2}$
δ^*	$\delta_{1,1}$	1	$\frac{1}{2}$
ν^*	$\nu_{\parallel}$	1	$\frac{1}{2}$
η^*	$\eta_{\parallel}+1$	2	3
d^*	$d-1$	1	3

when $N^* \to \infty$, $N_1 \to \infty$, and $T \neq T_c$. It is clear from Eq. (4.33) that in this limit we have

$$F^*(T, H_1) = F_s(T, H_1) , \tag{4.36}$$

where $F_s(T, H_1)$ is the surface free energy [Eq. (3.1)] in the presence of a field H_1 acting only on the surface. Thus we have separated the partition function of the half-space into the bulk partition function, plus that of a system of spins on the surface only, interacting via the temperature-dependent Hamiltonian $\mathcal{H}^*$, whose free energy is $F^* = F_s$. Since the field $H_1 \equiv H^*$ only couples to the surface spins it is clear that the magnetization

$$m^* = -\left(\frac{\partial F^*}{\partial H^*}\right)_T \tag{4.37}$$

is just the local magnetization m_1, and the susceptibility

$$\chi^* = \frac{\partial m^*}{\partial H^*} \tag{4.38}$$

is the quantity $\chi_{1,1}$ defined in Eq. (3.9). The correlation function $C^*(r^*, t, H^*)$ is of course $C_{\parallel}(\rho, t, H_1)$. Thus we have a correspondence between the surface system (denoted by starred quantities) whose interaction is complicated and even singular at T_c and the half-space studied in Secs. I–III. We may make a correspondence between critical exponents, as indicated in Table I.

The singular interaction in the surface system can lead to a different type of transition than in bulk systems; e.g., the entropy or internal energy may diverge at T_c. Nevertheless, we shall see in Sec. V B that the scaling properties are preserved, so that some of the exponents of the starred system may be inferred if others are known. In any event, the relations derived in Sec. IV are exact, since they only involve a formal rewriting of the partition function.

C. High- and Low-Temperature Expansions

For completeness, we mention here the exact expansions of the correlation function near a surface at high and low temperatures, which were reported recently by Fisher and Camp.[36] Let $\vec{r}' = (\vec{\rho}', z')$ and $\vec{r}'' = (\vec{\rho}'', z'')$ be two points in the system with $\rho \equiv |\vec{\rho}' - \vec{\rho}''|$, and let us specialize to $z' = z''$. This means that we consider only parallel correlations, but for an arbitrary layer z'. Then Fisher and Camp have shown that the correlation function can be written in the form

$$C(\rho, z') = D\rho^{-\Psi} F(\rho, z') e^{-\rho/\xi^{\times}}, \tag{4.39}$$

where D and Ψ are constants and where for high temperatures and $z' \ll \rho$ we have

$$F(\rho, z') \approx \rho\,(1 - e^{-(z'+a)^2/\epsilon\rho}), \tag{4.40}$$

with $\xi^{\times}$ and ϵ having dimensions of length.[39] For low temperatures Fisher and Camp find that the length $\xi^{\times}$ in Eq. (4.39) in larger than ξ_b, so the decay is slower. On the other hand, their result refers to the first terms in a power-series expansion, and it is not clear to us how these results apply near T_c. For the special case of the nearest-neighbor Ising half-plane, however, they confirm the results of MW discussed in Sec. IV A 2, namely, $\xi_{\parallel}^{>} = \xi_b^{>}$ for $t > 0$, and $\xi_{\parallel}^{<} = 2\xi_b^{<} = \xi_b^{>}$ for $t < 0$. Moreover, Fisher and Camp show that the exponent Ψ in Eq. (4.39) has the general form

$$\Psi^{>} = \tfrac{1}{2}(d-1) + d_{\perp}, \qquad t > 0 \tag{4.41a}$$

$$\Psi^{<} = \tfrac{1}{2}(d-1) - \tfrac{1}{2}d_{\perp}, \quad t < 0 \tag{4.41b}$$

where $d_{\perp} = 0$ for the bulk and $d_{\perp} = 1$ for the half-space. For $t > 0$ and $d = 2$, Eq. (4.41a) yields $\Psi^{>} = \frac{3}{2}$ in accordance with Eq. (4.16), but for $t < 0$ the term with $\Psi^{<} = 0$ obtained from Eq. (4.41b) has zero coefficient D and the next term has $\Psi^{>} = \frac{3}{2}$, in accordance with Eq. (4.16). A similar "accident" occurs in the bulk.[34–36]

V. SCALING THEORIES IN SYSTEMS WITH SURFACES

Scaling theories seem to be extremely accurate[1,13] (perhaps even exact!) for bulk Ising models in two and three dimensions. It is therefore interesting to attempt to generalize these theories to systems containing surfaces. Such generalizations are particularly desirable since they yield relations between critical exponents and permit estimates of otherwise unknown exponents in terms of calculated ones. We shall show examples of such scaling estimates in the following analysis.

A. Scaling in Finite Systems

Fisher[16] has presented a scaling theory applicable to our layered system. He considers, for example, the susceptibility $\chi(T, N_1)$ for finite thickness $N_1 \gg 1$ and writes it in the form

$$\chi(T, N_1) = N_1^{2-\eta} X(\dot{t} N_1^{1/\nu}) , \tag{5.1}$$

where

$$\dot{t} \equiv \frac{T - T_c(N_1)}{T_c(N_1)} = t + bN_1^{-\bar{\lambda}} , \tag{5.2}$$

$$t \equiv \frac{T - T_c(\infty)}{T_c(\infty)} . \tag{5.3}$$

Equation (5.2) defines a critical exponent $\bar{\lambda}$ (denoted λ by Fisher) representing the shift in transition temperature for finite thickness. [Of course, strictly speaking, the exponent $\bar{\lambda}$ is only defined by Eq. (5.2) for $d \geq 3$, since there is no transition in two-dimensional strips of finite thickness.] The scaling ansatz (5.1) implicitly assumes that the bulk correlation length is applicable to the finite system, i.e., roughly speaking, that $\nu_\perp = \nu_b$. From Eq. (5.1) Fisher concludes that the surface susceptibility exponent γ_s is either given by

$$\gamma_s = \gamma + \nu \tag{5.4}$$

or by

$$\gamma_s = \gamma + 1 . \tag{5.5}$$

The first case [Eq. (5.4)] holds if

$$\bar{\lambda} > 1, \tag{5.6}$$

and the second case [Eq. (5.5)] if

$$\bar{\lambda} = 1. \tag{5.7}$$

In the spherical model an exact calculation[14,16] yields

$$\bar{\lambda} = 1, \quad \nu_b = 1 \quad \text{for } d = 3 , \tag{5.8}$$

but

$$\bar{\lambda} = 1, \quad \nu_b = \tfrac{1}{2} \quad \text{for } d \geq 4, \tag{5.9}$$

with logarithmic corrections in the case $d = 4$. In the two-dimensional Ising model and the three-dimensional spherical model Eqs. (5.4) and (5.5) are indistinguishable, since $\nu_b = 1$, but the spherical model in higher dimensionality provides a concrete example for Eq. (5.5). The numerical results for the $d = 3$ Ising case[40] indicate that

$$\bar{\lambda} = \nu^{-1} > 1, \tag{5.10}$$

in accordance with Eq. (5.6), whereas[16] $\gamma_s = 1.95 \pm 0.08$, which is consistent with Eq. (5.6), $\gamma_s = \gamma + \nu = 1.89$. On the other hand, Monte Carlo studies[41] of finite three-dimensional cubes seem to be more consistent with $\bar{\lambda} = 1$. Both the thickness of the films[17] and the linear dimensions of the hypercubes[41] studied are probably too small to draw firm conclusions, so the situation is not entirely clear at present for the three-dimensional Ising model.

The phenomenological theory of Sec. II yields results which agree with both Eq. (5.9) and Eq. (5.10) [cf. Eqs. (2.24) and (2.30)]. As remarked earlier, the statement of Fisher[16] that $\bar{\lambda} = 1$ in mean-field theory only refers to the crudest estimates, and completely neglects the important effects of correlations which exist both in the phenomenological approach (Sec. II A) and the microscopic molecular-field approximation (Sec. II B 3).

B. Scaling for Surface Problem

In Sec. IV B we showed that the half-space can be exactly reduced to a surface problem with a complicated (singular) interaction between spins. It is natural to assume that this "starred" $(d-1)$-dimensional system satisfies scaling, i.e., that we may write

$$F^*(t^*, h^*) = |t^*|^{2-\alpha^*} f(t^*/|h^*|^{1/\beta^*\delta^*}), \tag{5.11}$$

$$C^*(r^*, t^*, h^*) = (r^*)^{-d^*+2-\eta^*} \Gamma[r^*/\xi^*(t), r^*/\zeta^*(h^*)], \tag{5.12}$$

where we have written

$$t^* = t = (T - T_c)/T_c \tag{5.13}$$

and

$$h^* = H^*/k_B T_c = H_1/k_B T_c = h_1 . \tag{5.14}$$

It follows from Eqs. (5.11) and (5.12) that the scaling laws hold:

$$2 - \alpha^* = \beta^*(\delta^* + 1) = \gamma^* + 2\beta^* = d^*\nu^* = 2\beta^* + \nu^*(2 - \eta^*) . \tag{5.15}$$

It might be objected that scaling need not apply to systems with long-range interactions (since these satisfy mean-field theory), and we do not know the precise form of the interaction function $V^*(\{\sigma^*\}, T)$ [Eq. (4.35)]. It turns out, however, that such a scaling of exponents for the surface system holds *exactly* in two dimensions, as can be seen from the transcription given in Table I ($\alpha^* = 1$, $\beta^* = \frac{1}{2}$, $\gamma^* = 0$, $\delta^* = 1$, $\nu^* = 1$, $\eta^* = 2$, $d^* = 1$). Moreover, the scaling of correlations, Eq. (5.12), has been verified in detail, as explained in Sec. IV A. Thus it is natural to assume that the scaling ansatz [(5.11) and (5.12)] will hold more generally, at least for $d = 3$ and $d = 4$, where it holds to a good approximation in the bulk. For $d = 4$, the bulk exponents reduce to those of molecular-field theory,[42] and it is natural to assume that the surface exponents do also, and to calculate the starred exponents for this case. From the exponents calculated in Sec. II A we have $\alpha^* = \alpha_s = \frac{1}{2}$, $\beta^* = \beta_1 = 1$, $\gamma^* = \gamma_{1,1} = -\frac{1}{2}$, $\delta^* = \delta_{1,1} = \frac{1}{2}$, $\nu^* = \nu_\parallel = \frac{1}{2}$, $\eta^* = \eta_\parallel + 1 = 3$, and for $d = 4$, $d^* = 3$. From these values we verify all the scaling relations (5.15) using the mean-field starred exponents for $d = 4$! The observation that scaling for starred exponents works exactly for $d = 2$, and also for $d = 4$ assuming mean-field behavior, indicates strongly that it will also be no worse than ordinary (bulk) scaling for $d = 3$. [Of course, the starred exponents in d dimensions bear no simple relationship to the bulk exponents in $(d-1)$ dimensions.] We shall use starred scaling to estimate exponents for $d = 3$ in Sec. VI B 3. Let us remark immediately, however, that if $\nu^* \equiv \nu_\parallel$

$=\nu_b=\nu$, we have $(d^*=d-1)$

$$2-\alpha^*=2-\alpha_s=d^*\,\nu^*=(d-1)\nu=d\nu-\nu=2-\alpha-\nu\,. \tag{5.16}$$

Note that in the formulation of scaling given in Eq. (5.1) the exponent ν seems to be more closely related to $\nu_\perp$, about which nothing is known exactly, even in two dimensions. Since Eq. (5.10) holds exactly in this case, the implication is that, at least for $d=2$, we have $\nu_\perp=\nu_\parallel=\nu$.

C. Inequality for γ_1

In this section we derive an inequality for the exponent γ_1 by remarking that

$$\chi_1=\sum_{\vec{r}} C_1(\vec{r})=\sum_{\vec{\rho}}\sum_{z=0}^{\infty} C_1(\vec{\rho},\,z)\,, \tag{5.17}$$

where

$$C_1(\vec{r})\equiv C(\vec{r}\,'=0,\,\vec{r})\,, \tag{5.18}$$

whereas

$$\chi_{3d}=\sum_{\vec{\rho}}\sum_{z=-\infty}^{\infty} C_b^{(3)}(\vec{\rho},z) \tag{5.19}$$

and

$$\chi_{2d}=\sum_{\vec{\rho}} C_b^{(2)}(\vec{\rho})\,. \tag{5.20}$$

Since the correlation function is (at least predominantly) a positive quantity, and $C_b^{(3)}\geq C_1\geq C_b^{(2)}$, we have

$$\chi_{3d}(T)\geq\chi_1(T)\geq\chi_{2d}(T)\,. \tag{5.21}$$

Let us now consider the quantity χ^{-1}/χ_0^{-1} as a function of T^{-1}. (χ_0 is the value of χ for $T\to\infty$.) We see (Fig. 3) that $\chi_1^{-1}(T)/\chi_0^{-1}$ must always lie above the $3d$ curve by Eq. (5.21). Since it crosses this curve both at $T=\infty$ and $T=(T_c)_{3d}$, we conclude that the critical exponent γ_1 (describing the rate at which χ_1^{-1}/χ_0^{-1} vanishes) must be less than the $3d$ exponent γ, i.e.,

$$\gamma_1\leq\gamma\,. \tag{5.22}$$

It is straightforward to generalize the above result to arbitrary χ_n, i.e.,

$$\gamma_n\leq\gamma\,. \tag{5.23}$$

Of course, the exponents to be derived in Sec. VI satisfy Eq. (5.22), as do the mean-field exponents (see Tables II and III).

D. Scaling of Correlation Function

In addition to the above scaling theories, which involve the surface exponents and the local exponents parallel to the boundary, it is interesting to ask how the correlation function between a surface spin and an interior spin behaves. For the bulk correlation function the scaling assumptions[13] can be written

$$C_b(\vec{r}\,',\,\vec{r}\,'',\,t)=r^{2-d-\eta}\,\Gamma_b[r/\xi(t)]\,, \tag{5.24}$$

where $r=|\vec{r}\,'-\vec{r}\,''|$. The simplest generalization of Eq. (5.24) for the correlation function $C_1(\vec{r},\,t)=C_1(r,\,\theta,\,t)=C_1(\vec{\rho},\,z,\,t)$ between a point $\vec{\rho}\,'=0$, $z'=0$ on the surface and a point $\vec{r}$ in the interior is the assumption

$$\text{Case (I): } C_1(r,\,\theta,\,t)=\frac{f_1(\theta)}{r^{d-2+\eta_{\min}}}\,\Gamma^{(1)}[r/\xi_\theta(t),\,\theta] +\frac{f_2(\theta)}{r^{d-2+\eta_{\min}+\delta\eta}}\,\Gamma^{(2)}[r/\xi_\theta(t),\,\theta]+\cdots\,, \tag{5.25}$$

where θ is the angle between $\vec{r}$ and the normal to the surface. Equation (5.25) implies that in each direction there exists a scaling of lengths, but with the possibility that the critical exponents may be different in different directions. For instance, if $f_1(\frac{1}{2}\pi)=0$ and $f_2(\frac{1}{2}\pi)\neq 0$, then $\eta_\perp=\eta_{\min}$, but $\eta_\parallel=\eta_{\min}+\delta\eta$. Note that under the assumption of Eq. (5.25), for smooth functions f_1 and f_2, the exponent η varies discontinuously with angle, having its minimum value almost everywhere and a higher value at those angles where $f_1(\theta)=0$ (for $\delta\eta>0$). Similarly, ξ_θ may have an exponent ν_θ which varies discontinuously with θ. In Appendix B we show that the correlation function C_1 has the form (5.25) in mean-field theory, and it seems likely to us that this behavior will hold in general. Another possibility, however, is that the critical exponent itself varies continuously with angle rather than the functions f_1 and f_2, i.e.,

$$C_1(r,\,\theta,\,t)=r^{2-d-\eta_\theta}\,\Gamma^{(3)}[r/\xi_\theta(t),\,\theta]\,, \tag{5.25a}$$

with η_θ, for instance, a smooth function of angle. This case, which seems somewhat unlikely to us, is also discussed briefly in Appendix B.

Another possibility is that there exists no scaling in arbitrary directions, i.e., that a change of

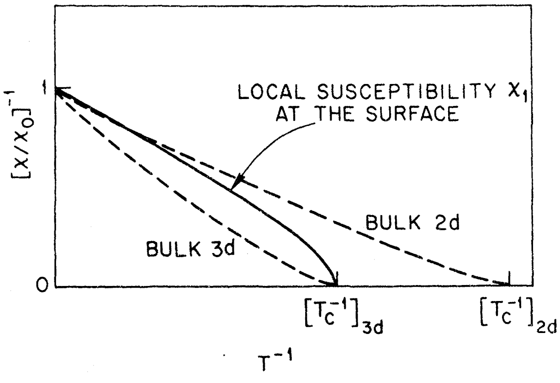

FIG. 3. Schematic drawing of the temperature dependence of the local susceptibility χ_1, normalized to its value χ_0 at infinite temperature. Also shown are the bulk susceptibilities χ for two and three dimensions. It is seen from this figure that $\gamma_1\leq\gamma_b(3d)$.

TABLE II. Summary of thermodynamic exponents in Ising half-space.

Quantity	Bulk magnetization	Layer magnetization	Bulk specific heat	Surface specific heat	Bulk susceptibility	Surface susceptibility
Symbol	m	m_1	C_b	C_s	χ	χ_s
Exponent	β	β_1	α	α_s	γ	γ_s
Ising $d=2$	$\frac{1}{8}^{a}$	$\frac{1}{2}$	0 (log)^{a}	1^{a}	$\frac{7}{4}^{a}$	$\frac{11}{4}^{b}$
Ising $d=3$	$\frac{5}{16}^{b}$	0.64^{c}	$\frac{1}{8}^{b}$	0.76^{c}	$\frac{5}{4}^{b}$	$1.96 \sim 2.0^{b}$
Mean field	$\frac{1}{2}$	1	0 (finite)	$\frac{1}{2}$	1	$\frac{3}{2}$

Quantity	Layer susceptibility	Local susceptibility	T_c shift	Local critical isotherm
Symbol	χ_1	$\chi_{1,1}$	ΔT_c	$m_1(h_1)$
Exponent	γ_1	$\gamma_{1,1}$	$\bar{\lambda}$	$\delta_{1,1}$
Ising $d=2$	$\frac{11}{8}^{b}$	0 (log)^{a}	$1^{a,d}$	1^{a}
Ising $d=3$	$\frac{7}{8}^{b}$	$0 \leq \gamma_{1,1} \leq \frac{1}{8}^{b}$	$\frac{3}{2}^{b}$	1^{c}
Mean field	$\frac{1}{2}$	$-\frac{1}{2}$	2	$\frac{1}{2}$

[a] Exact calculation.

[b] Numerical (series extrapolation).

[c] Scaling estimate.

[d] For $d=2$, $\bar{\lambda}$ is the exponent of the shift in the specific-heat maximum.

length cannot be compensated by a change in temperature, except in symmetry directions. In that case one might have an expression of the form

$$\text{Case (II): } C_1(r,\ \theta,\ t) = C_1(\vec{\rho},\ z,\ t)$$

$$= \frac{f_4(\theta)}{r^{d-2+\eta_{\min}}}\,\Gamma^{(4)}\left(\frac{z}{\xi_\perp(t)},\ \frac{\rho}{\xi_\parallel(t)}\right) + \frac{f_5(\theta)}{r^{d-2+\eta_{\min}+\delta\eta}}\,\Gamma^{(5)}\left(\frac{z}{\xi_\perp(t)},\ \frac{\rho}{\xi_\parallel(t)}\right) + \cdots, \tag{5.26}$$

with $\xi_\perp \propto t^{-\nu_\perp}$, $\xi_\parallel \propto t^{-\nu_\parallel}$, $\delta\nu = \nu_\perp - \nu_\parallel \gtrless 0$.

This latter possibility is less restrictive than case (I), and we mention it for completeness, although we have no reason to doubt the validity of the scaling form (I), Eq. (5.25). In Appendix B we show, under rather general assumptions concerning the θ dependences in Eq. (5.25), that this equation implies

$$\text{(I): } \gamma_1 = \nu_{\max}(2 - \eta_{\min}), \tag{5.27}$$

where the subscripts refer to maxima and minima over directions θ. In addition, we show that Eq. (5.25) implies

$$\text{(I): } \bar{\nu}_\parallel = \bar{\nu}_\perp = \nu_{\max}, \tag{5.28}$$

where $\bar{\nu}$ is the exponent for the effective correlation length defined in Eqs. (3.19)–(3.21).

Under the assumption (5.25a) we find

$$\gamma_1 = \max[\nu_\theta(2 - \eta_\theta)], \tag{5.29}$$

which is similar to Eq. (5.27) (see Appendix B).

For the scaling ansatz (II) [Eq. (5.26)], there is no simple scaling law analogous to Eq. (5.27), but for the effective exponents we have

$$\text{(II): } \bar{\nu}_\parallel = \nu_\parallel \tag{5.30}$$

and

$$\text{(II): } \bar{\nu}_\perp = \nu_\perp, \tag{5.31}$$

independent of whether $\nu_\parallel$ is greater or less than $\nu_\perp$.

In Sec. VI we shall describe numerical calculations of γ_1, $\bar{\nu}$, $\bar{\nu}_\perp$, and $\bar{\nu}_\parallel$ for both $d=2$ and $d=3$. We shall see that there is no evidence that ν depends on angle [so that case (II) above need not be considered], but that η_θ does depend on angle.

TABLE III. Summary of correlation exponents in Ising half-space.

Quantity	Bulk correlation range	Layer correlation range	Layer effective correlation range	Bulk correlations at T_c	Parallel correlations at T_c	Perpendicular correlations at T_c
Symbol	ξ	$\xi_\parallel$, $\xi_\perp$	$\bar{\xi}_\parallel$, $\bar{\xi}_\perp$, $\bar{\xi}$	$C(r)$	$C_\parallel(\rho)$	$C_\perp(z)$
Exponent	ν	$\nu_\parallel$, $\nu_\perp$	$\bar{\nu}_\parallel$, $\bar{\nu}_\perp$, $\bar{\nu}$	η	$\eta_\parallel$	$\eta_\perp$
Ising $d=2$	1^{a}	1^{a}, 1^{b}	1^{c}	$1/4^{a}$	1^{a}	$5/8^{b}$
Ising $d=3$	0.64^{c}	0.64^{b}	0.64^{c}	0.05^{c}	1^{b}	0.64^{b}
Mean field	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	2	1

[a] Exact calculation.

[b] Scaling estimate.

[c] Numerical (series extrapolation).

VI. EVALUATION OF CRITICAL EXPONENTS

A. Series Expansions

1. *Theoretical Method*

The general method for deriving Ising-model series expansions is well known,[43] and requires only simple formal modifications to include systems with free surfaces. The correlation function $C(\vec{r}\,', \vec{r}\,'+\vec{r}, t)$ is expanded in a series in the high-temperature parameter $v \equiv \tanh(2J/k_B T)$, with coefficients depending on $\vec{r}\,'$ and $\vec{r}$,

$$C(\vec{r}\,', \vec{r}\,'+\vec{r}, t) = v^{l_{\min}}[c_0(\vec{r}\,', \vec{r}) + c_2(\vec{r}\,', \vec{r})v^2 + c_4(\vec{r}\,', \vec{r})v^4 + \cdots], \qquad (6.1)$$

where $l_{\min}$ depends on the vector $\vec{r}$. In the bulk case the c_i of course depend only on $\vec{r}$, and for the half-space one can specialize the calculation to particular values of $\vec{r}\,'$, such as $\vec{r}\,'$ at the surface ($z'=0$), or $\vec{r}\,'$ on the first layer ($z'=a$), etc. In Appendix C we describe in detail the method used for obtaining the correlation coefficients $c_i(\vec{r}\,', \vec{r})$, and in Tables IV and V we list all the coefficients calculated, which are different from those in the bulk. Once the correlation coefficients are known, it is straightforward to calculate the coefficients for the susceptibilities $\chi_1, \chi_2, \ldots, \chi_{1,1}$, and χ_s using Eqs. (3.10)–(3.12), as well as those for the effective correlation range $\bar{\xi}_\parallel$, $\xi_\perp$, and $\bar{\xi}$ [cf. Eqs. (3.19)–(3.21)]. These coefficients are listed in Tables VI and VII, to tenth order for $d=2$ and to eighth order for $d=3$. For the extrapolation of the series the ratio method was used. Since in loose-packed lattices the ratios a_l/a_{l-1} of a series $\sum_{l=0}^{\infty} a_l v^l$ which is proportional to $t^{-\zeta}$ for $t \to 0$ show some "even-odd" oscillatory behavior, it is preferable to consider instead the quantities

$$(a_l/a_{l-2})^{1/2} \approx v_c^{-1}\left[\left(1+\frac{\zeta-1}{l}\right)\left(1+\frac{\zeta-1}{l-1}\right)\right]^{1/2} \approx \frac{1}{v_c}\left(1+\frac{\zeta-1}{[l(l-1)]^{1/2}}\right) \qquad (6.2)$$

[$v_c \equiv \tanh(2J/k_B T_c)$], which behave smoothly as a function of l. From the exact solution in $2d$, or from the longer series for the bulk susceptibility in $3d$, the critical point v_c is known to high accuracy, so our task consists of determining the critical exponent ζ. If the values of $(a_l/a_{l-2})^{1/2}$ as a function of l^{-1} {or $[l(l+1)]^{-1/2}$} fit a straight line going through v_c^{-1} at $l^{-1}=0$ {or $[l(l+1)]^{-1/2}=0$}, then the exponent ζ can be estimated as the slope of this line. In some cases (such as $\bar{\xi}$ and χ_s) there is considerable curvature present, and we have extrapolated the series $v^{\Delta}\sum_{l=0}^{\infty} a_l v^l$, which yields a straight line through v_c^{-1} for a suitably chosen Δ (in most cases $\Delta = -1$ was successful).

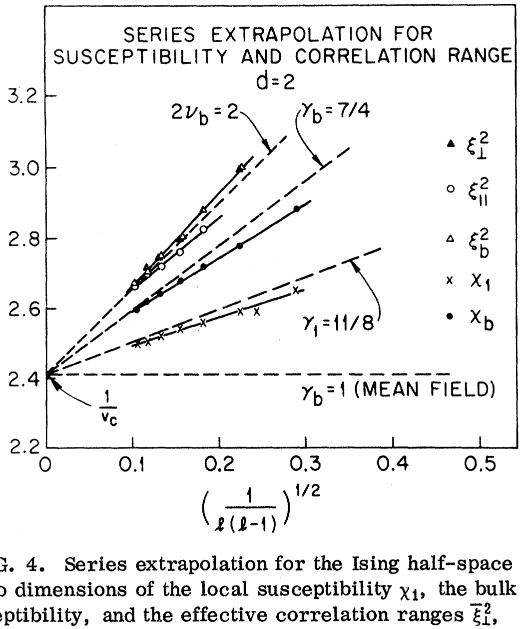

FIG. 4. Series extrapolation for the Ising half-space in two dimensions of the local susceptibility χ_1, the bulk susceptibility, and the effective correlation ranges $\bar{\xi}_\perp^2$, $\bar{\xi}_\parallel^2$, and $\bar{\xi}_b^2$. We conclude from these results that all the correlation exponents are the same for $d=2$.

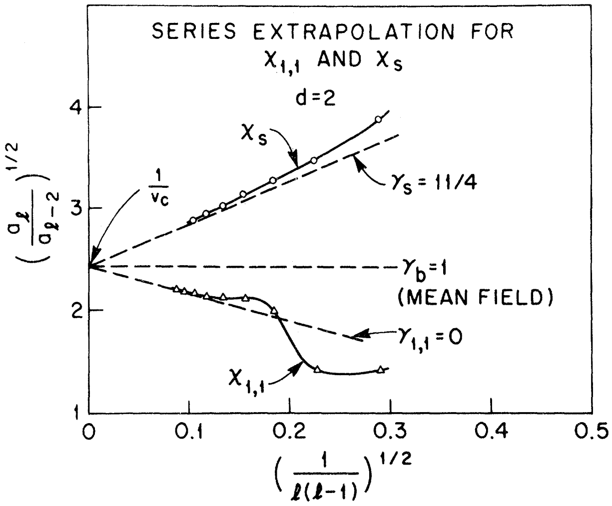

FIG. 5. Series extrapolation for $d=2$ of the local susceptibility $\chi_{1,1}$ and the surface susceptibility χ_s. The exact result of McCoy and Wu for $\chi_{1,1}$ is $\gamma_{1,1}=0$.

2. *Numerical Results for Exponents*

The results of the extrapolation procedures are illustrated in Figs. 4–7. We first show (Fig. 4), for $d=2$, the graphs for χ_1, $\bar{\xi}_\perp$, $\bar{\xi}_\parallel$, and we also show for comparison the series extrapolation of the bulk susceptibility and effective correlation length χ_b and $\bar{\xi}_b$, for which the exact exponents γ and ν are known. We conclude from Fig. 4 that $\gamma_1 = \frac{11}{8} \pm 0.05$, which is distinctly different from

$\gamma = \frac{7}{4}$. On the other hand, there is no evidence that $\overline{\nu}_{\parallel}$ or $\overline{\nu}_{\perp}$ is any different from $\nu = 1$. The quantities $\chi_{1,1}$ and χ_s for $d = 2$ are shown in Fig. 5, and we find $\gamma_{1,1} = 0$ and $\gamma_s = \frac{11}{4}$.

For $d = 3$, the corresponding results are shown in Figs. 6 and 7. Once again, although we find $\overline{\nu} \approx 0.7$, there is no serious evidence that $\overline{\nu}_{\perp}$, $\overline{\nu}_{\parallel}$, and $\overline{\nu}_b = 0.64$ are different, since the accuracy of the determination of $\overline{\nu}_{\parallel}$ and $\overline{\nu}_{\perp}$ is not very high. The other exponents are $\gamma_1 = \frac{7}{8}$, $\gamma_{1,1} = 0 \sim \frac{1}{8}$, and $\gamma_s \approx 2.0 \pm 0.08$. The above results are summarized in Tables II and III.

B. Scaling Estimates of Exponents

In this section we shall supplement the series-extrapolation results, which refer only to γ_1, $\gamma_{1,1}$, γ_s, $\overline{\nu}_{\parallel}$, $\overline{\nu}_{\perp}$, and $\overline{\nu}$, with scaling estimates for most of the other exponents.

TABLE IV. Correlation coefficients for $d = 2$. $\langle \sigma_{k,n}\, \sigma_{k+\Delta k, n+\Delta n} \rangle = \sum_l c_l v^l$. Only correlation coefficients c_l different from the bulk ones are shown.

l	$\Delta k, \Delta n$	1,0				0,1			2,1			1,2	
	k, n	1,1	1,2	1,3	1,4	1,1	1,2	1,3	1,1	1,2	1,3	1,1	1,2
1		1	1	1	1	1	1	1					
3		1	2	2	2	2	2	2	3	3	3	3	3
5		2	3	4	4	2	4	4	7	11	11	10	11
7		5	5	11	12	2	10	12	13	25	31	18	30
9		15	13	26	41	4	18	40	31	45	89	26	72
l	$\Delta k, \Delta n$	1,2	3,0			0,3		3,2		2,3		4,1	
	k, n	1,3	1,1	1,2	1,3	1,1	1,2	1,1	1,2	1,1	1,2	1,1	1,2
3		3	1	1	1	1	1						
5		11	6	12	12	12	12	10	10	10	10	5	5
7		31	19	33	48	42	48	40	55	49	55	32	52
9		96	57	42	124	86	146	101	173	131	193	108	188
l	$\Delta k, \Delta n$	1,4		5,0		0,5	4,3	3,4	5,2	2,5	6,1	1,6	7,0
	k, n	1,1	1,2	1,1	1,2	1,1	1,1	1,1	1,1	1,1	1,1	1,1	1,1
5		5	5	1	1	1							
7		51	52	15	30	30	35	35	21	21	7	7	1
9		208	243	90	180	240	203	231	161	223	93	148	28
l	$\Delta k, \Delta n$	1,1				2,0				0,2			2,2
	k, n	1,1	1,2	1,3	1,4	1,1	1,2	1,3	1,4	1,1	1,2	1,3	1,1
2		2	2	2	2	1	1	1	1	1	1	1	
4		3	4	4	4	3	6	6	6	6	6	6	6
6		4	9	10	10	7	11	16	16	12	16	16	19
8		8	19	31	32	19	17	39	46	16	42	46	39
10		26	27	92	117	59	76	77	149	18	92	152	72
l	$\Delta k, \Delta n$	2,2		3,1			1,3			4,0			0,4
	k, n	1,2	1,3	1,1	1,2	1,3	1,1	1,2	1,3	1,1	1,2	1,3	1,1
4		6	6	4	4	4	4	4	4	1	1	1	1
6		24	24	16	26	26	25	26	26	10	20	20	20
8		69	76	40	71	92	69	91	92	44	83	118	110
10		159	239	103	135	262	128	265	297	153	215	368	328
l	$\Delta k, \Delta n$	0,4	3,3		4,2		2,4		5,1		1,5		6,0
	k, n	1,2	1,1	1,2	1,1	1,2	1,1	1,2	1,1	1,2	1,1	1,2	1,1
4		1											
6		20	20	20	15	15	15	15	6	6	6	6	1
8		83	99	120	83	118	111	118	57	92	91	92	21
10		444	289	444	264	437	400	512	257	448	522	537	167
l	$\Delta k, \Delta n$	6,0	0,6	4,4	5,3	3,5	6,2	2,6	7,1	1,7	8,0		
	k, n	1,2	1,1	1,1	1,1	1,1	1,1	1,1	1,1	1,1	1,1		
6		1	1										
8		42	42	70	56	56	28	28	8	8	1		
10		348	462	476	406	496	290	407	142	225	36		

1. *Phenomenological Theory*

We have already seen in Sec. V B that the mean-field exponents satisfy starred scaling for $d=4$ and the other scaling relations,

$$\gamma_1 = \nu(2-\eta_{\min}) = \tfrac{1}{2}, \qquad (6.3)$$

$$\gamma_s = \gamma + \nu = \tfrac{3}{2}, \qquad (6.4)$$

$$\alpha_s = \alpha + \nu = \tfrac{1}{2}, \qquad (6.5)$$

are also satisfied.

2. *Two-Dimensional Case*

Here we first note that the series result $\gamma_{1,1}=0$ agrees with the exact result [Eq. (4.10)], which gives us confidence in the conclusions we draw from extrapolations of our relatively short series.

TABLE V. Correlation coefficients for $d=3$. Only correlation coefficients different from the bulk ones are shown. $\langle \sigma_{j,k,n}\, \sigma_{j+\Delta j,k+\Delta k,n+\Delta n}\rangle = \sum_l c_l v^l$.

l	$\Delta j, \Delta k, \Delta n$	1,0,0			0,0,1		1,1,1		2,1,0	
	j, k, n	1,1,1	1,1,2	1,1,3	1,1,1	1,1,2	1,1,1	1,1,2	1,1,1	1,1,2
1		1	1	1	1	1				
3		3	4	4	4	4	6	6	3	3
5		22	39	40	36	40	46	54	29	47
7		219	403	455	318	448	460	636	325	604
l	$\Delta j, \Delta k, \Delta n$	2,0,1		1,0,2		3,0,0		0,0,3	2,2,1	2,1,2
	j, k, n	1,1,1	1,1,2	1,1,1	1,1,2	1,1,1	1,1,2	1,1,1	1,1,1	1,1,1
3		3	3	3	3	1	1	1		
5		43	47	46	47	18	24	24	30	30
7		475	643	582	648	271	489	492	420	495
l	$\Delta j, \Delta k, \Delta n$	3,2,0	3,0,2	2,0,3	3,1,1	1,1,3	4,1,0	4,0,1	1,0,4	5,0,0
	j, k, n	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
5		10	10	10	20	20	5	5	5	1
7		205	340	349	350	418	127	182	201	45
l	$\Delta j, \Delta k, \Delta n$	1,1,0			1,0,1			2,0,0		
	j, k, n	1,1,1	1,1,2	1,1,3	1,1,1	1,1,2	1,1,3	1,1,1	1,1,2	1,1,3
2		2	2	2	2	2	2	1	1	1
4		10	16	16	15	16	16	9	12	12
6		88	160	170	132	169	170	95	171	176
8		976	1810	2130	1362	2061	2143	1081	2041	2341
l	$\Delta j, \Delta k, \Delta n$	0,0,2		2,2,0		2,0,2		2,1,1		1,1,2
	j, k, n	1,1,1	1,1,2	1,1,1	1,1,2	1,1,1	1,1,2	1,1,1	1,1,2	1,1,1
2		1	1							
4		12	12	6	6	6	6	12	12	12
6		168	176	84	144	139	144	138	168	158
8		1968	2340	1084	2062	1945	2265	1643	2361	2050
l	$\Delta j, \Delta k, \Delta n$	1,1,2	3,1,0		3,0,1		1,0,3		4,0,0	
	j, k, n	1,1,2	1,1,1	1,1,2	1,1,1	1,1,2	1,1,1	1,1,2	1,1,1	1,1,2
4		12	4	4	4	4	4	4	1	1
6		168	66	106	96	106	105	106	30	40
8		2410	974	1836	1424	1955	1871	1975	622	1121
l	$\Delta j, \Delta k, \Delta n$	0,0,4	2,2,2	3,2,1	3,1,2	2,1,3	3,3,0	3,0,3	4,1,1	1,1,4
	j, k, n	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1
4		1								
6		40	90	60	60	60	20	20	30	30
8		1140	1590	1130	1340	1417	540	939	761	922
l	$\Delta j, \Delta k, \Delta n$	4,2,0	4,0,2	2,0,4	5,1,0	5,0,1	1,0,5	6,0,0		
	j, k, n	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1	1,1,1		
6		15	15	15	6	6	6	1		
8		433	713	741	218	309	343	63		

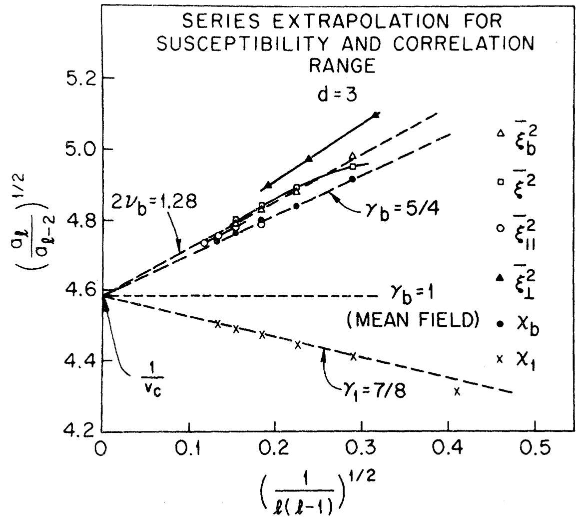

FIG. 6. Series extrapolation for the Ising half-space in three dimensions of the local susceptibility χ_1, the bulk susceptibility χ_b, and the correlation ranges $\bar{\xi}_\perp^2$, $\bar{\xi}_\parallel^2$, $\bar{\xi}_b^2$. There is again no reason to assume that any of the effective correlation exponents are different.

Concerning the correlations, we have the exact results $\nu_\parallel = 1 = \nu$ and the numerical results $\bar{\nu}_\parallel \cong \bar{\nu}_\perp \cong 1$. Thus scaling possibility (II) [Eqs. (5.30) and (5.31)] reduces to (I), and we have [Eq. (5.28)]

$$\bar{\nu} = \nu_{\max} = \nu_\parallel = 1 . \tag{6.6}$$

We therefore assume

$$\nu_\perp = \nu_\parallel = 1 , \tag{6.7}$$

since we consider the possibility

$$\nu_\perp < 1 \tag{6.8}$$

highly unlikely. Indeed, the scaling relations (5.5) and (5.16), $\gamma_s = \gamma + \nu$ and $\alpha_s = \alpha + \nu$, most probably involve $\nu_\perp$, and the results $\gamma_s = \frac{11}{4}$ and $\alpha_s = 1$ [Eq. (4.6)] imply $\nu_\perp = 1$. Thus we conclude that in two dimensions there is only one correlation length:

$$\bar{\nu} = \bar{\nu}_\perp = \bar{\nu}_\parallel = \nu_\perp = \nu_\parallel = \nu = 1. \tag{6.9}$$

It then follows from the scaling relation $\gamma_1 = \nu_{\max} \times (2 - \eta_{\min})$ [Eq. (5.27)] and Eq. (6.6) that

$$\eta_{\min} = \tfrac{5}{8} = \eta_\perp , \tag{6.10}$$

since $\eta_\parallel = 1$. It would be interesting to verify Eq. (6.10) by an exact calculation. This completes the estimate of the two-dimensional exponents, which are summarized in Tables II and III.

3. *Three-Dimensional Case*

In this case there are no exact results, and the series estimates are somewhat less accurate than in two dimensions. Nevertheless, it seems likely that in analogy to the two-dimensional case there is only one correlation length,

$$\nu_\parallel = \nu_\perp = \bar{\nu}_\parallel = \bar{\nu}_\perp = \nu = 0.64 \pm 0.05. \tag{6.11}$$

Then, from the value $\gamma_1 = \frac{7}{8}$ and the scaling relation (5.27), we find $\eta_{\min} \approx 0.64$ (note that this value is not, *a priori*, related to the value of ν). From the scaling law for starred exponents, $\gamma^* = \nu^* (2 - \eta^*)$, i.e., $\gamma_{1,1} = \nu_\parallel (1 - \eta_\parallel)$ (see Table I) and the calculated value $\gamma_{1,1} \approx 0$ from Fig. 7, we find

$$\eta_\parallel \approx 1, \tag{6.12}$$

which identifies $\eta_{\min}$ as $\eta_\perp$, i.e.,

$$\eta_{\min} = \eta_\perp = 0.64. \tag{6.13}$$

Further, from the scaling laws $2\beta^* + \gamma^* = 2 - \alpha^*$ [Eq. (5.15)] and $\alpha^* = \alpha_s = \alpha + \nu$ we find

$$\beta^* = \beta_1 = 0.64 \pm 0.08 , \tag{6.14}$$

which differs from the mean-field answer $\beta_1 = 1$ and from the generalized expression $\beta_1 = \beta + \nu \approx 1$ [Eq. (4.15)] obtained by assuming a temperature-independent extrapolation length.

The scaling result for the surface free energy F_s, namely, $\alpha_s = \alpha + \nu$, yields

$$\alpha_s = 0.765, \tag{6.15}$$

TABLE VI. Susceptibility coefficients for $d = 2$.

l	χ_b	χ_1	χ_2	χ_3	χ_s	$\chi_{1,1}$	$\bar{\xi}_b^2$	$\bar{\xi}_\parallel^2$	$2\bar{\xi}_\perp^2$
0	1	1	1	1	1	1	0	0	0
1	4	3	4	4	1	2	1	1	1
2	12	7	11	12	6	2	4	3	5
3	36	19	29	36	25	4	13	9	19
4	100	49	71	91	90	8	40	28	63
5	276	127	179	231	303	18	117	81	193
6	740	321	447	569	962	36	332	225	565
7	1972	815	1125	1411	2951	80	921	615	1603
8	5172	2041	2803	3473	8782	170	2512	1666	4451
9	13492	5117	6945	8582	25645	382	6757	4467	12153
10	34876	12763	17441	21167	73072	828	18004	11837	32763

and that for χ_s, $\gamma_s = \gamma + \nu$ yields

$$\gamma_s = 1.89\,, \tag{6.16}$$

which is lower than our direct calculation (cf. Fig. 7),

$$\gamma_s = 2.0 \pm 0.08\,. \tag{6.17}$$

Let us note that Allen[17] has estimated γ_s from slightly longer series for thin films, and he finds[16]

$$\gamma_s = 1.95 \pm 0.08\,, \tag{6.18}$$

which is in slightly better agreement with the scaling estimate (6.16), and tends to reinforce our conclusion that there is only one correlation-length exponent [Eq. (6.11)]. The results for $d=3$ are also listed in Tables II and III.

VII. CONCLUSION

We conclude by summarizing the principal results of this investigation.

(i) Phase transitions are studied in d-dimensional magnetic systems with free surfaces. A number of new critical exponents must be defined in order to describe the thermodynamic singularities and static correlations near the critical point (Sec. III). These exponents refer either to surface quantities or to local quantities. By a surface quantity we mean a contribution to the free energy which remains proportional to the number of spins on the free surface of a system as the total number of spins goes to infinity. A local quantity is the thermodynamic average of an operator defined at a point, e.g., the surface magnetization.

(ii) The phenomenological or mean-field theory is formulated quite generally, in terms of a boundary condition on the order parameter at the surface. This condition introduces a new length which is in general unknown, but which may be calculated in simple cases (Sec. II). Generally speaking, for magnetic systems this length is of the order of the interaction range $R \approx \xi_0$, in contrast to superconductors where the length is very much larger than ξ_0, due to specific properties of the electrons (Sec. II B4). The critical exponents are evaluated in the phenomonological theory.

(iii) The exact solution of the nearest-neighbor Ising half-plane derived by MW is discussed in detail (Sec. IV A) and related to the general formulation mentioned above. The critical exponents of this exact theory differ from those of the molecular-field theory.

(iv) An exact reformulation of the half-space is presented, whereby the system is separated into the bulk plus a pure $(d-1)$-dimensional surface problem, with a complicated temperature-dependent interaction between spins. The critical exponents of this surface problem (starred exponents) may be related to the previously defined exponents of the half-space (Sec. IV B).

(v) A scaling theory for the surface problem is shown to hold exactly for two dimensions, where the surface is a line. A similar scaling is assumed to hold in three dimensions, and yields relations between the exponents of the half-space (Sec. V B). These relations are also verified in molecular-field theory for $d=4$, so that the starred problem is a nontrivial three-dimensional model, all of whose exponents have been determined and shown to satisfy scaling exactly!

(vi) The scaling of correlations between a surface spin and a spin in the interior is also discussed. Due to the anisotropy introduced by the surface it is necessary to assume, in general, that the correlation exponents ν and η depend on direction. From the scaling assumption for the correlation function, additional exponent relations are found (Sec. V D).

(vii) Series expansions have been performed for the half-space to tenth order in two dimensions and to eighth order in three dimensions. A number of critical exponents are determined in this way, and agreement is found with the exact calculation of MW and with the scaling assumptions, wherever applicable (Sec. VI A). It is found that for both $d=2$ and $d=3$ the exponent ν is independent of direction, but η is strongly anisotropic. A similar situation holds in the phenomenological theory.

(viii) Using the numerical calculations and the various scaling assumptions, all the critical exponents for the three-dimensional Ising half-space have been estimated. This constitutes the central result of the present paper, and it is summarized in Tables II and III. The only previous estimates of these exponents were those of the molecular-field theory, and in many cases the differences are con-

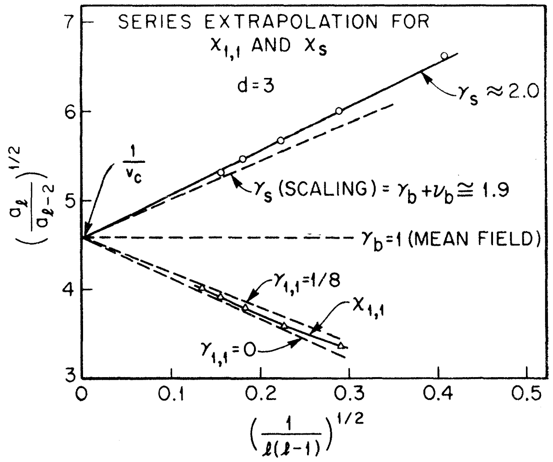

FIG. 7. Series extrapolation for $d=3$ of the local susceptibility $\chi_{1,1}$ and the surface susceptibility χ_s.

TABLE VII. Susceptibility coefficients for $d=3$.

l	χ_b	χ_1	χ_2	χ_3	χ_s	$\chi_{1,1}$	$\bar{\xi}_b^2$	$\bar{\xi}_\parallel^2$	$2\bar{\xi}_\perp^2$
0	1	1	1	1	1	1	0	0	0
1	6	5	6	6	1	4	1	1	1
2	30	21	29	30	10	12	6	5	7
3	150	93	137	149	71	40	31	23	41
4	726	409	621	709	440	136	156	110	223
5	3510	1837	2821	3341	2553	516	765	527	1153
6	16710	8209	12661	15409	14126	1968	3714	2519	5799
7	79494	36969	57185	70853	76071	7904	17827	11931	28593
8	375174	166041	257333	322865	399868	31756	85144	56534	139671

siderable.

(ix) The most promising experimental methods for testing some of the predictions of the present paper are Mössbauer or LEED measurements of the surface magnetization and LEED experiments on critical scattering from the surface.[9,9a,18,19] It must be noted, however, that all the numerical results were obtained under the assumption of ideal surfaces and in particular that the exchange interaction is unmodified by the surface. This condition is of course very difficult to verify in practice. Present experimental data[9a,19] seem to agree better with the mean-field result $\beta_1=1$ than with our result $\beta_1=\frac{2}{3}$, obtained for the case of equal interactions between all spins. The source of the discrepancy is not clear to us at the moment, but it could be due to experimental inaccuracies or to a significant weakening of the exchange interactions at the surface of the crystal. More experimental and theoretical work is needed to clarify the situation.

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APPENDIX A: REDUCTION TO PURE SURFACE PROBLEM

We begin with the Hamiltonian, Eq. (4.30), which we write explicitly as a sum over α and n with, in general, $i=(\alpha,n)$. Letting $\hat{\delta}^*$ be a nearest-neighbor vector within a layer, we have $(N=N_1N^*)$

$$\mathcal{H}=-J\sum_{n=1}^{N_1}\sum_{\alpha=1}^{N^*}\{\sigma_{\alpha,n}\sigma_{\alpha+\hat{\delta}^*,n}+\sigma_{\alpha,n}\sigma_{\alpha,n+1}+\sigma_{\alpha,n}\sigma_{\alpha,n-1}\}-H_1\sum_{\alpha=1}^{N^*}\sigma_{\alpha,1}\,, \tag{A1}$$

where by definition $\sigma_{\alpha,0}\equiv 0$. We define

$$\sigma_\alpha^*=\sigma_{\alpha,1}\,, \tag{A2}$$

and separate out the term with $n=1$ in Eq. (A1),

$$\mathcal{H}=-J\sum_{\alpha=1}^{N^*}\{\sigma_\alpha^*\sigma_{\alpha+\hat{\delta}^*}^*+2\sigma_\alpha^*\sigma_{\alpha,2}\}-J\sum_{n=2}^{N_1}\sum_{\beta=1}^{N^*}\{\sigma_{\beta,n}\sigma_{\beta+\hat{\delta}^*,n}+2\sigma_{\beta,n}\sigma_{\beta,n+1}\}-H_1\sum_{\alpha=1}^{N^*}\sigma_\alpha^*\,. \tag{A3}$$

The partition function, Eq. (4.31), is

$$Z(T,H_1)=2^{-N^*}\sum_{\{\sigma_\alpha^*=\pm1\}}\exp\left((k_BT)^{-1}\sum_{\alpha=1}^{N^*}[J\sigma_\alpha^*\sigma_{\alpha+\hat{\delta}^*}^*+H_1\sigma_\alpha^*+V(T,\{\sigma_\alpha^*\})]\right)\,, \tag{A4}$$

where

$$\exp((k_BT)^{-1}V(T,\{\sigma_\alpha^*\}))\equiv 2^{-(N-N^*)}\sum_{\{\sigma_{\beta,n}=\pm1\}}\exp\left((J/k_BT)\times\left[2\sigma_\alpha^*\sigma_{\alpha,2}+\sum_{n=2}^{\infty}\sum_{\beta=1}^{N^*}(\sigma_{\beta,n}\sigma_{\beta+\hat{\delta}^*,n}+2\sigma_{\beta,n}\sigma_{\beta,n+1})\right]\right)\,. \tag{A5}$$

In the limit $N_1\to\infty$, $N^*\to\infty$ the function $V(T,\{\sigma_\alpha^*\})$ is proportional to $NF_b(T)$, where F_b is the free energy per spin of the bulk system Eq. (3.1). There is, however, a correction of order N^*, which yields

$$V^*(T,\{\sigma_\alpha^*\})=\lim_{N^*\to\infty,N_1\to\infty}\left(\frac{1}{N^*}V(T,\{\sigma_\alpha^*\})-N_1F_b(T)\right)\,. \tag{A6}$$

The quantity V^* remains of order unity. We now may define a very complicated temperature-dependent Hamiltonian, but one involving only the spins σ_α^* in the surface,

$$\mathcal{H}^*=-J\sum_{\alpha=1}^{N^*}\sigma_\alpha^*\sigma_{\alpha+\hat{\delta}^*}^*+N^*V^*(T,\{\sigma_\alpha^*\})-H^*\sum_{\alpha=1}^{N^*}\sigma_\alpha^*\,, \tag{A7}$$

where we have written $H_1\equiv H^*$. The Hamiltonian $\mathcal{H}^*$ is of order N^*, and from Eqs. (A5)–(A7) and

(3.1) we see that its free energy

$$F^*(T,H^*)\equiv k_BT\ln Z^*(T,H^*)\,, \tag{A8}$$

$$Z^*(T,H^*)=2^{-N^*}\sum_{\{\sigma_\alpha^*=\pm 1\}} e^{-\mathcal{H}^*/k_BT} \tag{A9}$$

is just equal to $F_s(T,H_1)$, defined in Eq. (3.1), except that the field H_1 acts only on the surface,

$$F^*(T,H_1)=F_s(T,H_1)\,. \tag{A10}$$

APPENDIX B: SCALING RELATIONS FOR CORRELATION EXPONENTS

The scaling form (5.24) for the correlation function, which is assumed to hold in bulk, must be generalized to take into account the anisotropy introduced by the surface. As was shown in Sec. II, even in mean-field theory the exponents depend on direction, i.e., $\eta_{\parallel}\neq\eta_{\perp}$ [Eqs. (2.43) and (2.48)], and it is interesting to calculate the correlation function for arbitrary angle θ in this case. According to Eqs. (2.37), (2.36), and (2.33), we have, for $d=2$,

$$C_1(\rho,z,t)=\left(\frac{\lambda}{\pi}\right)\int_0^\infty dq\,\cos(q\rho)\,\frac{e^{-\gamma(q)z}}{1+\lambda\gamma(q)}\,, \tag{B1}$$

with

$$\gamma^2(q)=q^2+\xi^{-2}\,. \tag{B2}$$

In order to integrate Eq. (B1) we expand in λ and use an integral representation of the Bessel function,[44]

$$C_1(\rho,z,t)=(\lambda/\pi\xi)\sum_{n=0}^{\infty}\int_0^\infty dx\,\cos(x\rho/\xi)\,(-1)^n[(\lambda/\xi)(1+x^2)^{1/2}]^n\exp[-(z/\xi)(1+x^2)^{1/2}]\,, \tag{B3}$$

$$=(\lambda/\pi\xi)\sum_{n=0}^{\infty}\lambda^n\left(\frac{\partial}{\partial z}\right)^n\left(\frac{z}{(z^2+\rho^2)^{1/2}}K_1[(z^2+\rho^2)^{1/2}/\xi]\right)\,, \tag{B4}$$

which for $z/\lambda\to\infty$, $\rho/\lambda\to\infty$ becomes ($\rho=r\sin\theta$, $z=r\cos\theta$)

$$C_1(\rho,z,t)=(\lambda/\pi\xi)[\cos\theta K_1(r/\xi)+(\lambda/r)\sin^2\theta K_1(r/\xi)+(\lambda/\xi)\cos^2\theta K_1'(r/\xi)+\cdots]\,. \tag{B5}$$

It is easy to verify that in the limits $\theta=0$ and $\theta=\frac{1}{2}\pi$ Eq. (B5) reduces to Eqs. (2.46) and (2.41), respectively.

The result in Eq. (B5) shows that for all angles $\theta\neq\frac{1}{2}\pi$ we have $\eta_\theta=1$, but for $\theta=\frac{1}{2}\pi$, $\eta_{\pi/2}=\eta_{\parallel}=2$. It is natural to assume this type of behavior in general, as in Eq. (5.25), and a similar form for the correlation length

$$\xi_0(t)=g_1(\theta)\,t^{-\nu_{\max}}+g_2(\theta)\,t^{-(\nu_{\max}-\delta\nu)}\,, \tag{B6}$$

with $\delta\nu>0$. Let us for concreteness assume that in Eq. (5.25) we have

$$f_1(\tfrac{1}{2}\pi)=0,\qquad f_1(0)\neq 0,\qquad f_2(\tfrac{1}{2}\pi)\neq 0\,, \tag{B7}$$

and calculate the susceptibility χ_1. According to Eqs. (3.10) and (5.25) we have, for $d=3$,

$$\chi_1=4\pi\int_0^{\pi/2}d\theta\,\cos\theta\,\{f_1(\theta)\int_0^\infty dr\,r^{1-\eta_{\min}}\Gamma^{(1)}[r/\xi_\theta(t),\theta]$$
$$+f_2(\theta)\int_0^\infty dr\,r^{1-\eta_{\min}-\delta\eta}\Gamma^{(2)}[r/\xi_\theta(t),\theta]\}\,. \tag{B8}$$

Substituting $x=r/\xi_\theta(t)$ we find

$$\chi_1=t^{-\nu_{\max}(2-\eta_{\min})}\int_0^{\pi/2}d\theta\,\cos\theta[g_1(\theta)+g_2(\theta)\,t^{\delta\nu}]^{2-\eta_{\min}}f_1(\theta)G_1(\theta)$$
$$+t^{-\nu_{\max}(2-\eta_{\min}-\delta\eta)}\int_0^{\pi/2}d\theta\,\cos\theta[g_1(\theta)+g_2(\theta)t^{\delta\nu}]^{2-\eta_{\min}-\delta\eta}f_2(\theta)G_2(\theta)+\cdots\,, \tag{B9}$$

where

$$G_i(\theta)=4\pi\int_0^\infty dx\,x^{1-\eta_{\min}}\Gamma^{(i)}(x,\,\theta)\,. \tag{B10}$$

Since there is no reason for any of the above integrals to vanish identically we find in general

$$\gamma_1=\nu_{\max}(2-\eta_{\min})\,. \tag{B11}$$

Clearly this result will also hold if $\eta_{\min}\neq\eta_{\perp}$ [cf. Eq. (B7)], since we can measure angles from an arbitrary direction. The moments of the correlation function may be calculated in similar fashion:

$$\left.\begin{matrix}\langle\rho^2\rangle\\ \langle z^2\rangle\end{matrix}\right\}=(4\pi)\int_0^{\pi/2}d\theta\,\cos\theta\left\{\begin{matrix}\sin^2\theta\\ \cos^2\theta\end{matrix}\right\}\{f_1(\theta)\int_0^\infty dr\,r^{3-\eta_{\min}}\Gamma^{(1)}[r/\xi_\theta(t),\,\theta]+f_2(\theta)\int_0^\infty dr\,r^{3-\eta_{\min}-\delta\eta}\Gamma^{(2)}[r/\xi_\theta(t),\,\theta]+\cdots\}\,, \tag{B12}$$

whence

$$\left.\begin{matrix}\langle \rho^2\rangle \\ \langle z^2\rangle\end{matrix}\right\} \propto t^{-\nu_{\max}(4-\eta_{\min})} , \tag{B13}$$

and by Eqs. (3.19) and (3.20) we have

$$\bar{\nu}_{\parallel} = \bar{\nu}_{\perp} = \nu_{\max} . \tag{B14}$$

If there is a direction with a smaller true exponent than the maximal one [i.e., if in Eq. (B6) we have $g_{\perp}(\theta_{\min}) = 0$], then for this direction the true and effective correlation exponents disagree.

For the case of continuously varying exponents, as in Eq. (5.25a), we may also calculate γ_1. Let us assume a correlation length of the form

$$\xi_\theta(t) = \xi_0 t^{-\nu_\theta} , \tag{B15}$$

with ν_θ a smooth function. Then we have

$$\chi_1 = 4\pi \int_0^{\pi/2} d\theta \cos\theta \int_0^\infty dr\, r^{1-\eta_\theta} \Gamma^{(3)}[r/\xi_\theta(t),\ \theta] , \tag{B16}$$

and, putting $x = r/\xi_\theta(t)$,

$$\chi_1 = \int_0^{\pi/2} d\theta \cos\theta\, \xi_0^{2-\eta_\theta} G_3(\theta) t^{-\nu_\theta(2-\eta_\theta)} , \tag{B17}$$

where

$$G_3(\theta) = 4\pi \int_0^\infty dx\, x^{1-\eta_\theta} \Gamma^{(3)}(x,\ \theta) \tag{B18}$$

is a bounded and regular function of θ. Now the integral in Eq. (B16) can be evaluated using the method of steepest descent,[45] yielding

$$\chi_1 \underset{t\to 0}{\sim} t^{-\max[\nu_\theta(2-\eta_\theta)]} \tag{B19}$$

or

$$\gamma_1 = \max[\nu_\theta(2-\eta_\theta)] . \tag{B20}$$

This result agrees with Eq. (B11) above, since in that case $\eta_\theta = \eta_{\min}$ and $\nu_\theta = \nu_{\max}$ almost everywhere, and $\max[\nu_\theta(2-\eta_\theta)] = \nu_{\max}(2-\eta_{\min})$.

Let us now discuss briefly the other scaling possibility, (II), Eq. (5.26), using the variables $u = \rho/\xi_\parallel$, $v = z/\xi_\perp$ (for $d = 3$),

$$\chi_1 = (2\pi)\xi_\parallel^2 \xi_\perp \int_0^\infty du\, u \int_0^\infty dv\, [f_4(ut^{\delta\nu}/v)\Gamma^{(4)}(u,\ v)(u^2\xi_\parallel^2 + v^2\xi_\perp^2)^{-1/2(1+\eta_{\min})} + f_5(ut^{\delta\nu}/v)\Gamma^{(5)}(u,\ v)(u^2\xi_\parallel^2 + u^2\xi_\perp^2)^{-1/2(1+\eta_{\min}+\delta\eta)} + \cdots] . \tag{B21}$$

An inspection of Eq. (B21) shows that the leading asymptotic behavior of χ_1 will depend both on the relative magnitudes of $\xi_\parallel$ and $\xi_\perp$ (i.e., on the sign of $\delta\nu$) and on the precise behavior of the function $f_4(x)$ for small and large x. Thus many different cases must be considered and no simple behavior emerges. For the effective exponents $\bar{\nu}_\parallel$ and $\bar{\nu}_\perp$, on the other hand, it is straightforward to verify that for reasonable functions [$f_i(x)$ and $\Gamma^{(i)}(u,\ v)$] these agree with the true exponents, i.e.,

$$\bar{\nu}_\parallel = \nu_\parallel , \tag{B22a}$$

$$\bar{\nu}_\perp = \nu_\perp . \tag{B22b}$$

As mentioned in the text, there is no evidence at present that the exponent ν_θ has any angular dependence, so the different cases considered here may not need to be distinguished, and the results of Eqs. (B11) and (B20) reduce to

$$\gamma_1 = \nu(2-\eta_{\min}) . \tag{B23}$$

APPENDIX C: SERIES EXPANSIONS FOR ISING SYSTEMS WITH FREE SURFACES

Consider a large cube of size $N = N^* N_1$ with two free surfaces, which is periodic in the other $(d-1)$ dimensions (Fig. 1). This system can be used to derive series expansions for films, if N_1 is small enough, and to derive series expansions of local quantities near a surface, if N_1 is sufficiently large (one takes the limit $N_1 \to \infty$ as the last step of the calculation, considering quantities at fixed positions near one of the two free surfaces).

Consider a spin correlation function

$$\langle \sigma_{\vec{r}\,'} \sigma_{\vec{r}\,'+\vec{r}} \rangle = \frac{\mathrm{Tr} \exp[(2J/k_B T)\sum_{\langle ij\rangle} \sigma_i \sigma_j] \sigma_{\vec{r}\,'} \sigma_{\vec{r}\,'+\vec{r}}}{\mathrm{Tr} \exp[(2J/k_B T)\sum_{\langle ij\rangle} \sigma_i \sigma_j]} , \tag{C1}$$

with $\sigma_i = \pm 1$ and with the brackets $\langle ij\rangle$ meaning that each pair of nearest neighbors i, j is counted once. As usual we make use of the identity

$$\exp[(2J/k_B T)\sigma_i \sigma_j] = \cosh(2J/k_B T) \times [1 + \sigma_i \sigma_j \tanh(2J/k_B T)] , \tag{C2}$$

and get, writing $v \equiv \tanh(2J/k_B T)$,

$$\langle \sigma_{\vec{r}\,'} \sigma_{\vec{r}\,'+\vec{r}} \rangle = \frac{\mathrm{Tr} \prod_{\langle ij\rangle} [1 + (\sigma_i \sigma_j) v](\sigma_{\vec{r}\,'} \sigma_{\vec{r}\,'+\vec{r}})}{\mathrm{Tr} \prod_{\langle ij\rangle} [1 + (\sigma_i \sigma_j) v]} . \tag{C3}$$

If any index i occurs an odd number of times in a term of the product of the denominator, this term will vanish on performing the trace. This leads to a graphical prescription for the series expansion of the denominator, associating with each term

$(\sigma_i\sigma_j)v$ a line connecting two vertices i, j and writing

$$\mathrm{Tr}\prod_{\langle ij\rangle}[1+(\sigma_i\sigma_j)v]=\sum_{l=0}^{\infty}P_N(l)v^l \quad [P_N(0)\equiv 1] , \tag{C4}$$

where $P_N(l)$ denotes the total number of graphs with l lines in the lattice which have only even vertices and where each nearest-neighbor bond of the lattice is used at most only once. (Note that a vertex is called even if an even number of lines meet at this vertex.) The graphs which are to be considered are polygons on the lattice (which can consist also of disconnected parts). The effect of the free surfaces enters in this expansion only in the actual counting of the $P_N(l)$'s. Similarly one gets for the numerator

$$\mathrm{Tr}\prod_{\langle ij\rangle}[1+(\sigma_i\sigma_j)v](\sigma_{\vec{r}'}\sigma_{\vec{r}'+\vec{r}})=\sum_{l=0}^{\infty}Q_{N,\vec{r}',\vec{r}}(l)v^l . \tag{C5}$$

$Q_{N,\vec{r}',\vec{r}}(l)$ denotes the total number of graphs in the lattice with l lines and only even vertices except the vertices $\vec{r}'$ and $\vec{r}+\vec{r}'$, which are odd vertices. Again each bond of the lattice has to be used (at most) only once. The typical graphs that are to be considered are chains (which can be linked to polygons). The numbers $Q_{N,\vec{r}',\vec{r}}$ depend also on $\vec{r}'$ and not only on $\vec{r}$, as in the bulk case. It is well known that the disconnected diagrams which lead to divergent terms in the limit $N\to\infty$ in both series in Eqs. (C4) and (C5) cancel out when the ratio equation (C3) is taken, making excluded volume corrections necessary. (For a thorough discussion of this point see Ref. 43.) As mentioned above, we obtain the final results by keeping $\vec{r}'$ fixed near the surface and then letting $N_1\to\infty$. The actual enumeration of graphs was performed in the case of the quadratic (2d) and simple-cubic (3d) lattices only. No triangles occur in these cases and thus the actual expansion for $\langle\sigma_{\vec{r}'}\sigma_{\vec{r}'+\vec{r}}\rangle$ is

$$\begin{aligned}\langle\sigma_{\vec{r}'}\,\sigma_{\vec{r}'+\vec{r}}\rangle=v^{l_{\min}}\{&Q_{N,\vec{r}',\vec{r}}(l_{\min})+Q_{N,\vec{r}',\vec{r}}(l_{\min}+2)\,v^2+[Q_{N,\vec{r}',\vec{r}}(l_{\min}+4)-P_N(4)\,Q_{N,\vec{r}',\vec{r}}(l_{\min})]\,v^4\\&+[Q_{N,\vec{r}',\vec{r}}(l_{\min}+6)-Q_{N,\vec{r}',\vec{r}}(l_{\min}+2)P_N(4)-Q_{N,\vec{r}',\vec{r}}(l_{\min})P_N(6)]\,v^6+(Q_{N,\vec{r}',\vec{r}}(l_{\min}+8)-Q_{N,\vec{r}',\vec{r}}(l_{\min}+4)P_N(4)\\&-Q_{N,\vec{r}',\vec{r}}(l_{\min}+2)P_N(6)-Q_{N,\vec{r}',\vec{r}}(l_{\min})P_N(8)+Q_{N,\vec{r}',\vec{r}}(l_{\min})[P_N(4)]^2)\,v^8+\cdots\} ,\end{aligned} \tag{C6}$$

where the power of the leading term $l_{\min}$ is simply given by

$$\vec{r}\equiv\begin{cases}(\Delta k,\Delta n)\quad(d=2): & l_{\min}=\Delta k+\Delta n\\(\Delta j,\Delta k,\Delta n)\quad(d=3): & l_{\min}=\Delta j+\Delta k+\Delta n .\end{cases} \tag{C7}$$

From Eq. (C6) one actually sees on doing the counting that disconnected diagrams cancel out. In the coefficient of $v^{l_{\min}+4}$ one has to consider the overlap of the chain $Q_{N,\vec{r}',\vec{r}}(l_{\min})$ with the square $P_N(4)$; in the coefficient of $v^{l_{\min}+6}$ one has to consider the overlap of the chain $Q_{N,\vec{r}',\vec{r}}(l_{\min}+2)$ with the square $P_N(4)$ and the overlap of the chain $Q_{N,\vec{r}',\vec{r}}\times(l_{\min})$ and the hexagon $P_N(6)$. The next term is considerably more involved; one has also to consider the overlap of three diagrams, namely, the chain $Q_{N,\vec{r}',\vec{r}}(l_{\min})$ and the two squares $P_N(4)$, and one must also take care of counting correctly the disconnected diagrams of $P_N(8)$ [= two squares $P_N(4)$], in which both parts overlap with the chain $Q_{N,\vec{r}',\vec{r}}(l_{\min})$. These complications are the reason that no higher-order terms than v^{10} ($d=2$) and v^8 ($d=3$) have been calculated. Note that in contrast to the bulk case one has to repeat the procedure for a variety of $\vec{r}'$ values (e.g., we have to put $\vec{r}'$ in all the rows 1, 2, ..., 10 for $d=2$ for at least some of the graphs, depending upon what $\vec{r}$ is considered). Putting $\vec{r}'$ more towards the interior of the system one recovers the bulk case; all bulk correlation coefficients have also been calculated and the complete agreement with the corresponding results of Fisher and Burford[46] (Appendix B, Tables XVI and XVII of Ref. 46) served as a check for the correctness of the counting procedures.

The counting of graphs was performed as follows: As a first step we count all the connected diagrams on the computer by a "systematic drawing procedure." All the coordinates of a $N=(N^*)^d$ system ($N^*\approx 10-20$ is sufficient in our case) are kept in the storage. The coordinates of $\vec{r}'$ and $\vec{r}$ and the number of lines l are specified. Now the program starts a drawing procedure going from $\vec{r}'$ to one of its nearest neighbors ($\hat{=}$ "drawing" the first line), from these to a nearest neighbor of this place ($\hat{=}$ "drawing" the second line), and so on. Only such lattice points are considered at each drawing step of the procedure, at which there still remains the possibility that one can get to the point $\vec{r}'+\vec{r}$ with the remaining number of lines (i.e., the intermediate points must not be too remote). This restriction is essential for getting reasonable computing times (our total time needed for all $\vec{r}'$'s, $\vec{r}$'s and $d=2$ and $d=3$ was about 20 min on the IBM 360/91 of the Institut für Plasmaphysik, Garching). Immediate reversals in the drawing procedure are, of course, forbidden. The vertices of the graph which is drawn step by step are labeled and stored, and if one gets in the course of the procedure to some vertex a second (third, etc.) time, it is easy to find which bonds ending at this vertex are already occupied (a second use of these is forbidden). This trial drawing is successful if it is possible to reach $\vec{r}' + \vec{r}$ in spite of the various restrictions. The surface plane acts simply as a geometrical restriction. This drawing procedure has to be systematically repeated, and thus the total number of possible graphs is counted. One must take care of the overcounting, however. Everything is correct for simple chains or simple polygons (which are counted by taking $\vec{r} = 0$). If one has precisely one fourfold vertex in the graph occurring, it is simple to recognize that this graph is just counted twice, so that there is no difficulty in correcting for this overcounting. In the case of higher-order connected diagrams (one sixfold vertex, or two fourfold vertices, etc.) it was found convenient to store these lines explicitly, and any new graph is compared to the previously stored ones: If it turns out that the graph is identical to one of them the new graph is abandoned, while otherwise the new graph is added into storage. Since only rather low orders in the series expansion were calculated, only a small number of these highly connected diagrams could occur, and therefore such straightforward procedures as described above were sufficient. Also, it was sufficient to count the overlaps of lower-order disconnected diagrams by hand, using the $Q_{N,\vec{r}',\vec{r}}(l_{\min})$, $Q_{N,\vec{r}',\vec{r}}(l_{\min}+2)$, $Q_{N,\vec{r}',\vec{r}}(l_{\min}+4)$, $P_N(4)$, $P_N(6)$, and $P_N(8)$ which had been calculated explicitly by the computer program. It is clear that the explicit drawing of overlaps by hand would already be too tedious in the ninth order ($d=3$) or the eleventh order ($d=2$), respectively. In this case one would have to consider a far more sophisticated programming also to count the overlaps (or at least most types of them) on the computer. These problems are discussed in more detail by Fisher and Burford.[46] More recently, renormalized linked-cluster expansions[47] have been successfully used to derive higher-order terms of series expansions, and this technique also seems preferable if one wants to extend the present investigation to a semi-infinite Heisenberg model.

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$$C_{\parallel}(\tilde{\rho}) = a\pi^{-1} \int_0^{\pi/a} dq \cos q\tilde{\rho}\, (4 - 2\cos qa - e^{-\gamma(q)a})^{-1},$$

$$\cosh\gamma(q)a = 2(1+t) - \cos qa.$$

Then we may integrate by parts twice and show that the term of order $\tilde{\rho}^{-1}$ vanishes, and that the term of order $\tilde{\rho}^{-2}$ coincides with Eq. (2.42a), for $t=0$, say. This specific microscopic calculation demonstrates that there is no contribution to Eq. (2.40) from the upper cutoff at $q_c \approx \xi_0^{-1}$.

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[29] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill, New York, 1953), p. 981. We are indebted to U. Schotte and D. Schotte and to W. Götze for informative discussions on this problem.

[30] Ref. 16, Sec. 5.4.

[31] Ref. 29, p. 982. Note that there is a misprint in the statement of the integral equation solved. The factor $\frac{1}{2}$ should be absent from the argument of the hyperbolic cosine.

[32] D. G. Naugle and R. E. Glover, Phys. Letters 28A, 110 (1968); D. G. Naugle, R. E. Glover III, and W. Moormann, in *Superconductivity, Proceedings of the International Conference on the Science of Superconductivity, Stanford, California*, 1969, edited by F. Chilton (North-Holland, Amsterdam, 1971), p. 250.

[33] The general results of MW may be simplified for equal interactions between rows and columns and for $t \to 0$, $h_1 \to 0$ as follows:

$$z_1(t) = z_2(t) = \tanh(2J/k_BT) \equiv \tanh(E_1/k_BT).$$

At $t=0$, $z_{1c} \equiv c^{-1} = \sqrt{2}-1$; $z_{1c}^2 + 2z_{1c} - 1 = 0$. Also, at $t=0$, $\alpha_1 = \alpha_{1c} = z_{1c}^2$, $1-\alpha_{1c} = 2c^{-1}$. The critical temperature is given by

$$2J/k_BT_c = -\tfrac{1}{2}\ln z_{1c} \equiv \tfrac{1}{4}\bar{c} = \tfrac{1}{2}\ln(\sqrt{2}+1).$$

Thus, $z_1(t) = z_{1c}(1-\frac{1}{2}\bar{c}t)$ and $\alpha_2 = 1+\bar{c}t$. The magnetic field occurs in the form $z = \tanh h_1 \sim h_1$ for $h_1 \ll 1$.

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[38] The second term in the square brackets in Eq. (4.18) is of relative order $\rho^{-1}(\rho/\xi_\parallel)^2$ compared to the first, when $\rho \gg \xi_\parallel$, and it is not negligible when $(\rho/\xi_\parallel) \gg \rho^{1/2} \gg 1$. On the other hand, the subsequent terms must also contribute in this region in order to yield Eq. (4.16), which holds for fixed t (or $\xi_\parallel$) as $\rho \to \infty$. The precise nature of the cancellation is not clear, so that the strong scaling property cannot be considered to be proved rigorously. On the other hand, there is no reason to believe that in the bulk case the situation is any simpler. In the opposite limit, $\rho \ll \xi_\parallel$, the second term in the square brackets of Eq. (4.18) is of relative order $\xi^{-1} \ll 1$ compared to the terms in Eq. (4.20b). A similar situation holds in the bulk [see Eq. (8.13) of Ref. 34].

[39] The form (4.39) and (4.40) has the property that the bulk behavior is not restored until the condition $z' \gg (\rho\epsilon)^{1/2}$ is satisfied (note that $z' \ll \rho$). At high temperatures, where ξ is of microscopic dimensions, one might expect bulk behavior to be found for $z' \gg \xi \sim a$. Indeed, from the scaling analysis presented in Sec. V, one might conjecture that $C(\rho, z')$ would be of the form

$$C(\rho, z') = C_b(\rho)\,[1 + O(e^{-z'/\xi^\times})].$$

Since at high temperatures $\xi^\times = \xi_b$, which is proportional to the small parameter $v \equiv \tanh(2J/k_BT)$, it is not clear how the behavior in the above equation would show up in an expansion in v. We therefore do not understand the precise relationship of these exact high- and low-temperature results to the scaling analysis.

[40] Ref. 16, Fig. 12.

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[45] We are indebted to M. E. Fisher for a helpful discussion of this point.

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