Semi-infinite systems with first-order bulk transitions

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Semi-infinite systems are considered which undergo a first-order transition. The global phase diagram is discussed within the framework of Landau theory. Several types of phase transitions are found. At some of these transitions, critical surface phenomena occur since a variety of surface exponents may be defined although there are no bulk exponents.

I. INTRODUCTION

The presence of a free surface strongly affects the phase diagram of a physical system. This influence has been primarily investigated for semi-infinite systems which undergo a *second*-order bulk transition.[1] From a theoretical point of view, the standard example is the semi-infinite Ising model. In space dimension $d=2$, exact results are available.[2-6] For $d>2$, mean-field theory,[7-9] Landau theory,[10,11] scaling phenomenology,[8,12] Monte Carlo simulations,[8] real-space renormalization-group methods,[13-16] and field-theoretic renormalization-group methods[17-21] have been applied to this problem. As a result, both the global phase diagram of the semi-infinite Ising model and the details of the various transitions are now thoroughly understood. Some aspects of the theoretical picture have also been verified by experiments. In particular, the critical-surface exponent β_1 which governs the scaling behavior of the surface order parameter has been determined for the ordinary transition in the antiferromagnet NiO by low-energy electron diffraction (LEED),[7,22,23] and in the ferromagnet Ni by spin-polarized LEED.[24]

On the other hand, many materials undergo a *first*-order transition in the bulk. Since there are no critical exponents at such a transition, the bulk behavior seems to be not particularly interesting from a theoretical or from an experimental viewpoint. However, this situation may change drastically as soon as one considers *surface* instead of bulk phenomena. As will be shown below, there are some transitions of the semi-infinite system where the surface becomes "critical," i.e., where surface quantities behave continuously or diverge although the bulk quantities are discontinuous.[25] Some aspects of these critical-surface phenomena which may be called critical-surface-induced disordering have been reported previously.[26,27]

Throughout this paper, we will use the framework of Landau theory as discussed in Sec. II. When applied to semi-infinite systems with a first-order bulk transition, several types of phase transitions are obtained. In this paper we explicitly discuss two models which are distinguished by different Landau expansions for the free energy. For these models, most quantities of interest can be calculated in closed form. In order to organize the results in a transparent way, we first summarize the results for the global phase diagram in Sec. III (see Fig. 2 below). At the bulk transition temperature $T=T^*$, there are two extraordinary transitions, E^+ and E^-, and two ordinary transitions, O_1 and O_2. The transitions O_1 and O_2 are separated by a multicritical point $\bar{s}$ (we use a terminology closely related to that used for the semi-infinite Ising model).[1,10,14] In addition, there is a surface transition S in the high-temperature regime with $T>T^*$. The various transitions may be most easily characterized by the behavior of the order parameter M_1 at the surface which is discussed in Sec. IV. In particular, it is found that M_1 goes to zero continuously at the transitions $\bar{s}$ and O_2. In Sec. V order-parameter profiles $M(z)$ are calculated in closed form for all values of the Landau coefficients. As the various transitions at $T=T^*$ are approached, these order-parameter profiles develop a specific shape (see Fig. 3 below). In Sec. VI surface free energies are evaluated, and in Sec. VII, experimental aspects and further theoretical problems are briefly discussed. Results for various surface susceptibilities are given in Appendix B.

II. LANDAU THEORY

Consider a d-dimensional semi-infinite system with a $(d-1)$-dimensional free surface. The coordinate perpendicular to the surface is denoted by z. The surface is given by the plane $z=0$. The $d-1$ Cartesian coordinates parallel to the surface are denoted by $\vec{\rho}$. The system is described by a scalar order parameter with a Landau free-energy functional of the general form,

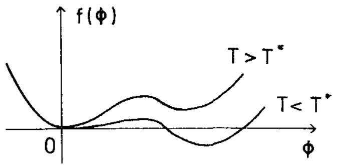

FIG. 1. Generic shape of bulk term $f(\phi)$ in the Landau free energy for a first-order bulk transition.

$$F\{\phi\}=\int d^{d-1}\rho \int_0^\infty dz[\tfrac{1}{2}(\nabla\phi)^2+f(\phi)+\delta(z)f_1(\phi)]\ , \quad (1)$$

for the scalar field $\phi(\vec{\rho},z)$. The bulk properties of this model are governed by the term $f(\phi)$. Since we want to study first-order bulk transitions, $f(\phi)$ has the generic shape depicted in Fig. 1. Within Landau theory, the bulk order is described by the bulk order parameter $\phi=M_B$ which corresponds to the global minimum of $f(\phi)$ (see Fig. 1). At the transition temperature $T=T^*$, the disordered state with $\phi=0$ and the ordered state with $\phi=M_B^*>0$ coexist. For $T>T^*$, the system is in its disordered state with $M_B=0$, and for $T<T^*$, it is in its ordered state with $M_B>0$

Since the translational invariance is broken by the free surface, the order parameter $M=\langle\phi\rangle$ depends on the distance z from the surface. Thus the states of the semi-infinite system may be described in terms of order-parameter profiles $M(z)$. Within Landau theory, these profiles are obtained from the variational principle $\delta F\{\phi\}/\delta\phi=0$ with $\phi(\vec{\rho},z)=M(z)$. This leads to the differential equation,

$$\frac{d^2M}{dz^2}=\frac{\partial f(M)}{\partial M}\ , \quad (2)$$

together with the boundary condition,

$$\left.\frac{dM}{dz}\right|_{z=0}=\left.\frac{\partial f_1(M)}{\partial M}\right|_{M=M(z=0)}\ , \quad (3)$$

at the surface $z=0$. In the following, we abbreviate $M(z=0)\equiv M_1$. For large z, $M(z)$ must approach the value M_B of the order parameter in the bulk. Thus one has to impose the additional boundary condition,

$$\lim_{z\to\infty} M(z)=M_B\ . \quad (4)$$

The Landau equation (2) has the form of the classical equation of motion for a particle with coordinate $M(z)$ moving in a one-dimensional potential $-f(M)$. Conservation of energy and the boundary condition (4) imply

$$\frac{1}{2}\left[\frac{dM}{dz}\right]^2-f(M)=-f(M_B)\ .$$

Thus one has

$$\frac{dM}{dz}=\begin{cases}+[2f(M)-2f(M_B)]^{1/2}\ , & M_1<M_B\\ -[2f(M)-2f(M_B)]^{1/2}\ , & M_1>M_B\end{cases} \quad (5)$$

with the initial value $M(z=0)\equiv M_1$ which is determined by (3).

A combination of (3) and (5) yields

$$\frac{\partial f_1(M_1)}{\partial M_1}=\begin{cases}+[2f(M_1)-2f(M_B)]^{1/2}\ , & M_1<M_B\\ -[2f(M_1)-2f(M_B)]^{1/2}\ , & M_1>M_B\end{cases} \quad (6)$$

which is an implicit equation for M_1. In general, this equation may have several solutions. Each solution for M_1 will yield a profile $M(z)$ when used as an initial value for the differential equation (5). In order to choose the unique profile which describes the equilibrium state, one must consider the surface free energy f_s

The Landau expression for this quantity is

$$f_s=f_1(M_1)+\int_0^\infty dz\left[\frac{dM}{dz}\right]^2\ . \quad (7)$$

The equilibrium value for $M(z)$ corresponds to the minimum of f_s.

So far, the discussion has been quite general: Many of the features which will be discussed below do not depend on the specific form of the functions $f(M)$ and $f_1(M)$, but derive only from the fact that the bulk transition is first order. On the other hand, it is instructive to consider the simplest model where (5) can be solved analytically. This model is defined by

$$f(\phi)=-h\phi+\tfrac{1}{2}a\phi^2-\frac{1}{x}b\phi^x+\frac{1}{y}c\phi^y\ , \quad (8a)$$

$$f_1(\phi)=-h_1\phi+\tfrac{1}{2}a_1\phi^2\ , \quad (8b)$$

with $b,c>0$ and with integer exponents $[x,y]=[3,4]$ or $[x,y]=[4,6]$. Only infinitesimal symmetry-breaking fields $h,h_1\geq 0$ will be considered in order to discuss various susceptibilities (see Appendix B).

For finite h,h_1, the phase diagram is more complex since additional lines of interface delocalization transitions are present in this case.[27] The phase diagram becomes also more complex if higher-order terms such as, e.g., ϕ^3 are included in the surface term (8b).[26,27]

Model (8) with $[x,y]=[3,4]$ is applicable to systems which allow a cubic invariant such as the q-state Potts model. [For $(d,q)=(3,3)$, the discontinuous nature of the bulk transition is now well established.[28-30]] If the cubic term is not allowed because of symmetry, one is led to consider model (8) with $[x,y]=[4,6]$. All systems which have a bulk tricritical point belong to this class. The tricritical bulk transition occurs for $a=b=0$ in (8a). The corresponding semi-infinite case has been investigated by Landau theory[31,32] and by field-theoretic renormalization.[32] Here we are concerned with $a,b>0$ where the bulk transition is first order.

As usual, we assume that the dominant temperature dependence is contained in the Landau coefficient a which enters the bulk term $f(\phi)$. The remaining coefficients are taken to be temperature independent. The coefficient a_1 which enters the surface term $f_1(\phi)$ is related to the relative strength of microscopic interaction parameters in the bulk and in the surface. For example, one may consider the semi-infinite q-state Potts model on a lattice where two Potts spins interact in the bulk and in the surface via the coupling constants J and J_1, respectively.[25,33,34] If one performs the continuum limit in the usual way, one finds[35]

$$a_1=1-2(d-1)(J_1/J-1)$$

as for the semi-infinite Ising model. Thus a_1 is positive when $J_1 \ll J$, and a_1 is negative when $J_1 \gg J$.

III. GLOBAL PHASE DIAGRAM

First consider the infinite bulk system. The first-order bulk transition occurs at

$$a=a^*=\begin{cases}2b^2/(9c)\ , & [x,y]=[3,4]\\ 3b^2/(16c)\ , & [x,y]=[4,6]\end{cases} \tag{9}$$

which corresponds to the bulk transition temperature $T=T^*$. Accordingly, the temperature deviation is proportional to

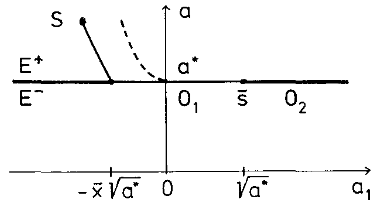

FIG. 2. Global (a,a_1) phase diagram. $a=a^*$ corresponds to the bulk transition temperature $T=T^*$. The different types of phase transitions are denoted by S, E^+, E^-, O_1, $\bar{s}$, and O_2. The dashed line is a line of metastability.

$$\delta a \equiv a-a^* \propto T-T^*\ . \tag{10}$$

In the ordered phase below T^*, the bulk order parameter is given by

$$M_B=\begin{cases}\dfrac{1}{2c}[b+(b^2-4ac)^{1/2}]\ , & [x,y]=[3,4]\\ \left[\dfrac{1}{2c}[b+(b^2-4ac)^{1/2}]\right]^{1/2}\ , & [x,y]=[4,6]\end{cases} \tag{11a}$$

At $T=T^*$ ($a=a^*$), M_B jumps from

$$M_B^*=\begin{cases}2b/(3c)\ , & [x,y]=[3,4]\\ [3b/(4c)]^{1/2}\ , & [x,y]=[4,6]\end{cases} \tag{11b}$$

to zero. In the semi-infinite case, we obtain several phase transitions which are schematically shown in the global (a,a_1) phase diagram of Fig. 2 with $h=h_1=0$. (The case with finite symmetry-breaking fields h,h_1 will be discussed elsewhere.) First, consider the dashed line in the high-temperature regime with $a>a^*$ which is given by

$$a_1=\bar{\bar{a}}_1(a)=-\sqrt{\delta a}\ . \tag{12}$$

This line separates the region with $M(z)=0$ ($a>a^*, a_1>\bar{\bar{a}}_1$) from the region with two metastable profiles ($a>a^*, a_1<\bar{\bar{a}}_1$). One of these metastable profiles becomes the equilibrium profile at the phase boundary S (see Fig. 2). This phase boundary is given by the implicit equation $f_s=0$ which has to be solved numerically. However, it is possible to find the analytic form for S in the vicinity of $a=a^*$ [see (41a) below]. The result is

$$\tilde{a}_1(a)=\begin{cases}-\bar{x}(a^*)^{1/2}+\dfrac{1}{(1+\bar{x})^2}\dfrac{1}{(a^*)^{1/2}}\delta a\ln(\delta a)\ , & [x,y]=[3,4]\\ -\bar{x}(a^*)^{1/2}+\dfrac{1}{2(1+\bar{x})}\dfrac{1}{(a^*)^{1/2}}\delta a\ln(\delta a)\ , & [x,y]=[4,6]\end{cases} \tag{13a}$$

with

$$\bar{x}=\begin{cases}2^{1/3}-1\ , & [x,y]=[3,4]\\ 2^{1/2}-1\ , & [x,y]=[4,6]\end{cases} \tag{13b}$$

to leading order in δa. The next term is of $O(\delta a)$ At $a=a^*$, five different types of transitions occur (see Fig. 2). For $a_1<-\bar{x}(a^*)^{1/2}$, the extraordinary transition E^+ occurs if the line $a=a^*$ is approached from above while the transition E^- occurs if the same line is approached from below. For $a=a^*$ and $a_1>-\bar{x}(a^*)^{1/2}$, there are two ordinary transitions denoted by O_1 and O_2 which are separated by the multicritical point $\bar{s}$ with coordinates $(a,a_1)=[a^*,(a^*)^{1/2}]$ (see Fig. 2).

It is instructive to compare the phase diagram just described with the phase diagram of the semi-infinite Ising model where the bulk transition is continuous. In this case, the transition S is also continuous (note that this transition is only present for $d>2$ (see, e.g., Ref. 16). As a consequence, the transition line $\tilde{a}_1(a)$ and the line of metastability $\bar{a}_1(a)$ are identical in the Ising case. In addition, there is no difference between E^+ and E^-, and there is only one ordinary transition O.[11]

IV. SURFACE ORDER PARAMETER M_1

The various transitions at $a=a^*$ may be most easily distinguished by the behavior of the surface order parameter M_1. This quantity has to be found from the implicit equation (6). It is not possible to solve this algebraic equation for all values of $a<a^*$, but one can expand around $a=a^*$. First, consider model (8) with $[x,y]=[3,4]$. In this case, one finds for $a_1\geq(a^*)^{1/2}$,

$$M_1=\begin{cases}\dfrac{M_B^*}{(a_1^2-a^*)^{1/2}}\,|\delta a|^{1/2}+O(|\delta a|) \text{ for } O_2 & (14a)\\ \left[\dfrac{M_B^*}{c}\right]^{1/3}|\delta a|^{1/3}+O(|\delta a|^{2/3}) \text{ for } \bar{s} & (14b)\end{cases}$$

as the transition line $a=a^*$ is approached from below [δa has been defined in (10)]. For $a_1\geq(a^*)^{1/2}$ and $a>a^*$, $M_1=0$. Therefore M_1 behaves continuously at the transitions $\bar{s}$ and O_2 as

$$M_1\propto|T-T^*|^{\beta_1} \tag{15a}$$

with the surface exponent,[26]

$$\beta_1=\begin{cases}\frac{1}{2} \text{ for } O_2\\ \frac{1}{3} \text{ for } \bar{s}\end{cases} \tag{15b}$$

although the bulk order parameter M_B is discontinuous. For $a_1<(a^*)^{1/2}$, M_1 has the limiting behavior,

$$M_1=\left[\frac{2}{c}\right]^{1/2}[(a^*)^{1/2}-a_1]+O(\delta a) \text{ for } O_1,E^- \tag{16}$$

as $a=a^*$ is approached from below.

In the high-temperature regime $a>a^*$, the Landau equation (6) can be solved for all values of (a,a_1). There is always the solution $M_1=0$. For $a_1<\bar{a}_1(a)$ [compare (12)], there are two additional solutions,

$$M_1^{\pm}=M_B^*\pm\left[M_B^{*2}+\frac{2}{c}(a_1^2-a)\right]^{1/2}.$$

It can be shown analytically that the surface free energy as given by (7) has the property

$$f_s(M_1^+)<f_s(M_1^-)\ .$$

Thus M_1^- may be discarded and the relevant solution is

$$M_1=M_B^*+\left[M_B^{*2}+\frac{2}{c}(a_1^2-a)\right]^{1/2} \tag{17a}$$

for $a_1<\tilde{a}_1(a)$ [compare (13a)], and $M_1=0$ for $a_1>\tilde{a}_1(a)$. (17a) implies for $a\to a^*+0$,

$$M_1=\left[\frac{2}{c}\right]^{1/2}[(a^*)^{1/2}-a_1]+O(\delta a) \text{ for } E^+\ . \tag{17b}$$

Thus M_1 is continuous at E^- and E^+. Only at the transition O_1, M_1 behaves like the bulk order parameter M_B since in this case it jumps from the limiting value (16) for $a<a^*$ to zero for $a>a^*$

For model (8) with $[x,y]=[4,6]$, very similar results are found. At O_2 and $\bar{s}$, M_1 goes continuously to zero:

$$M_1=\begin{cases}\dfrac{M_B^*}{(a_1^2-a^*)^{1/2}}\,|\delta a|^{1/2}+O(|\delta a|^{3/2}) \text{ for } O_2 & (18a)\\ \left[\dfrac{3}{2c}\right]^{1/4}|\delta a|^{1/4}+O(|\delta a|^{3/4}) \text{ for } \bar{s}. & (18b)\end{cases}$$

Thus the surface exponent β_1 is now given by[26]

$$\beta_1=\begin{cases}\frac{1}{2} \text{ for } O_2\\ \frac{1}{4} \text{ for } \bar{s}\ .\end{cases} \tag{19}$$

Note that β_1 has the same value at the transition O_2 for both $[x,y]=[3,4]$ and $[x,y]=[4,6]$ while it differs at the transition $\bar{s}$. This also holds if various generalizations of (8) are considered.[26,27] At O_1 and E^-, M_1 has the limiting value,

$$M_1=\left[\left[\frac{3}{c}\right]^{1/2}[(a^*)^{1/2}-a_1]\right]^{1/2}+O(\delta a)\ . \tag{20}$$

In the high-temperature regime $a>a^*$, one finds $M_1=0$ for $a_1>\tilde{a}_1(a)$ [compare (13a)] and

$$M_1=\left[M_B^{*2}+\left[M_B^{*4}+\frac{3}{c}(a_1^2-a)\right]^{1/2}\right]^{1/2} \tag{21a}$$

for $a_1<\tilde{a}_1(a)$, which leads to

$$M_1=\left[\left[\frac{3}{c}\right]^{1/2}[(a^*)^{1/2}-a_1]\right]^{1/2}+O(\delta a)$$

$$\text{for } E^+\ . \tag{21b}$$

Thus in both models M_1 is continuous at E^- and E^+, discontinuous at O_1, and goes continuously to zero at $\bar{s}$ and O_2

V. ORDER-PARAMETER PROFILES $M(z)$

The order-parameter profile $M(z)$ is obtained from the differential equation (5). For model (8), this equation may be solved analytically. First, consider the case $[x,y]=[3,4]$. In the low-temperature regime $a<a^*$, one obtains

$$M(z)=M_B-\frac{2P}{Q+\sqrt{R}\sinh(\pm\sqrt{P}z+S)}\ , \tag{22a}$$

where the plus sign applies to $a_1>0$ while the minus sign applies to $a_1<0$. For $a_1=0$, one obtains a flat profile $M(z)=M_B$. The parameters in (22a) are

$$P=bM_B-2a\ , \tag{22b}$$

$$Q=c(2M_B-M_B^*)\ , \tag{22c}$$

$$R=\tfrac{2}{3}bc(M_B-M_B^*)\ , \tag{22d}$$

$$S=\operatorname{arcsinh}\left[\frac{1}{\sqrt{R}}\left[\frac{2P}{M_B-M_1}-Q\right]\right]\ . \tag{22e}$$

Note that the "initial value" M_1 enters the profile $M(z)$ only via the parameter S in (22e).

At the various transitions E^-, O_1, $\bar{s}$, and O_2, the profile $M(z)$ as given by (22a) develops a characteristic shape which is schematically shown in Figs. 3(a)-3(c). At E^-, the profile decreases monotonically to the value M_B of the bulk order parameter [see Fig. 3(c)]. At O_1, the profile either decreases [for $-\bar{x}(a^*)^{1/2}<a_1<0$] or increases [for $0<a_1<(a^*)^{1/2}$] monotonically to the value M_B [see Figs. 3(b) and 3(c)] [for $a_1=0$, $M(z)=M_B$ as mentioned before].

At these transitions, the length scale for the variation of $M(z)$ is given by the limiting value of $1/\sqrt{P}$ which is $1/(a^*)^{1/2}$. In contrast, a new length scale $\hat{l}$ appears at the transitions $\bar{s}$ and O_2 as shown in Fig. 3(a). At $z=\hat{l}$, the order-parameter profile $M(z)$ has a point of inflection. $\hat{l}$ can be calculated from the implicit equation $M(\hat{l})=\bar{M}$, where $\bar{M}$ corresponds to the local maximum of $f(M)$ (compare Fig. 1). Thus there is an interface which separates a disordered surface layer with $M(z)\gtrsim 0$ from the ordered bulk with $M(z)\lesssim M_B$.[25,26] This interface becomes delocalized since

$$\hat{l}=\frac{1}{(a^*)^{1/2}}\,|\ln M_1|+O(1)$$

$$=\frac{1}{(a^*)^{1/2}}\beta_1\,|\ln|\delta a||+O(1)\quad\text{for } O_2,\bar{s}\ . \tag{23}$$

The divergence of the length scale $\hat{l}$ induces a singular behavior in the excess quantity,

$$M_s=\int_0^\infty dz[M_B-M(z)]\quad\text{for } a<a^*\ . \tag{24}$$

A simple estimate of M_s for $a\to a^*-0$ gives[26]

$$M_s\simeq\int_0^{\hat{l}}dz\,M_B^*=M_B^*\hat{l}\ . \tag{25}$$

This is indeed the leading-order term since an explicit calculation yields

$$M_s=\left[\frac{2}{c}\right]^{1/2}\left[\ln(\sqrt{2cP}+Q)-\ln\left[\sqrt{2c}\frac{a_1M_1}{M_B-M_1}-\bar{A}\right]\right]\ , \tag{26a}$$

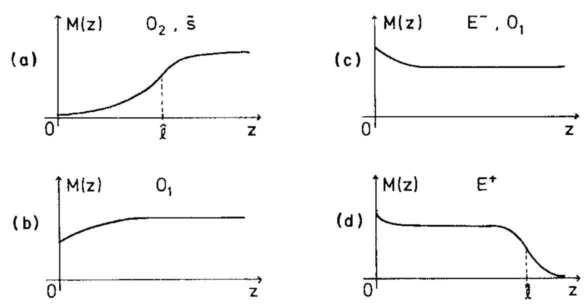

FIG. 3. Generic shapes of the order-parameter profile $M(z)$: (a) at the transitions O_2 and $\bar{s}$; (b) and. (c) at the transitions O_1 and E^-; (d) at the transition E^+. Near O_2, $\bar{s}$, and E^+ there is an interface at $z=\hat{l}$ and at $z=\hat{\hat{l}}$, respectively.

$$\bar{A}=-c(M_1+M_B)+\tfrac{2}{3}b \tag{26b}$$

for $a<a^*$ which implies

$$M_s=\left[\frac{2}{c}\right]^{1/2}\beta_1\,|\ln|\delta a||+O(1) \quad \text{for } O_2,\bar{s} \tag{27}$$

where the surface exponent β_1 is given by (15b). By analogy with the semi-infinite Ising model, we define the surface exponent β_s via $M_s \propto |T-T^*|^{\beta_s}$ This implies for the diverging length scale

$$\hat{l}\propto M_s \propto |T-T^*|^{\beta_s} \tag{28}$$

with the classical value $\beta_s=0$ (ln)

In the high-temperature regime with $a>a^*$ and $a_1<\tilde{a}_1(a)$, one obtains from(5) ($[x,y]=[3,4]$),

$$M(z)=\frac{2a}{\frac{2}{3}b+\sqrt{\bar{R}}\,\sinh(\sqrt{a}z+\bar{S})}\,, \tag{29a}$$

with

$$\bar{R}=2c(a-a^*)\,, \tag{29b}$$

$$\bar{S}=\text{arcsinh}\left[\frac{1}{\sqrt{\bar{R}}}\left[\frac{2a}{M_1}-\frac{2}{3}b\right]\right]. \tag{29c}$$

The initial value M_1 which enters the expression for $M(z)$ only via $\bar{S}$ in (29c) is given by (17a). As E^+ is approached, this profile has the characteristic shape shown in Fig. 3(d). In this case, there is an interface at a new length scale $z=\hat{l}$ which separates an ordered surface layer from the disordered bulk. $\hat{l}$ is obtained from $M(\hat{l})=\bar{M}$, where $\bar{M}$ corresponds to the local maximum of $f(M)$ (compare Fig. 1). This interface becomes delocalized at E^+ since

$$\hat{l}=\frac{1}{(a^*)^{1/2}}\,|\ln(\delta a)|+O(1) \quad \text{for } E^+\,. \tag{30}$$

This diverging length scale again induces a singularity in the excess quantity M_s, which is now defined by

$$M_s=\int_0^\infty dz\,M(z) \quad \text{for } a>a^*\,. \tag{31}$$

Changing variables from z to $M(z)$, one immediately obtains

$$M_s=\left[\frac{2}{c}\right]^{1/2}(\ln(\sqrt{2c}\,|a_1|+cM_1-\tfrac{2}{3}b)-\ln\{\sqrt{2c}\,[\sqrt{a}-(a^*)^{1/2}]\})\,, \tag{32a}$$

with the limiting behavior,

$$M_s=\left[\frac{2}{c}\right]^{1/2}|\ln(\delta a)|+O(1)=M_B^*\hat{l}+O(1) \quad \text{for } E^+\,. \tag{32b}$$

Thus at the transitions E^+, $\bar{s}$, and O_2, an interface appears which becomes delocalized as the bulk transition temperature $T=T^*$ is approached. This interface delocalization is due to the possible coexistence at $T=T^*$ of the disordered phase with one of the ordered phases. Such a delocalization phenomenon has also been found in the wetting[36-38] and in the pinning transition[39-43] where the interface delocalization is due to the possible coexistence of two ordered phases.

For model (8) with $[x,y]=[4,6]$, a very similar behavior is obtained. In the low-temperature regime with $a<a^*$, one finds

$$M(z)=M_B\left[\frac{R}{-\frac{1}{2}M_B^2+Q\coth^2(\sqrt{P}z+S_>)}\right]^{1/2} \tag{33}$$

for $a_1>0$, and

$$M(z)=M_B\left[\frac{R}{-\frac{1}{2}M_B^2+Q\tanh^2(\sqrt{P}z+S_<)}\right]^{1/2} \tag{34}$$

for $a_1<0$ with

$$P=\tfrac{1}{2}bM_B^2-a\,, \tag{33'a}$$

$$Q=\tfrac{3}{2}M_B^2-M_B^{*2}\,, \tag{33'b}$$

$$R=M_B^2-M_B^{*2}\,, \tag{33'c}$$

$$S_>=\text{arccoth}\left[\left[\frac{1+2R/M_1^2}{1+2R/M_B^2}\right]^{1/2}\right], \tag{33'd}$$

$$S_<=\text{arctanh}\left[\left[\frac{1+2R/M_1^2}{1+2R/M_B^2}\right]^{1/2}\right]. \tag{34'}$$

At the various transitions O_2, $\bar{s}$, O_1, and E^-, the limiting behavior of $M(z)$ is again given by the schematic curves in Figs. 3(a)-3(c).

In the high-temperature regime with $a>a^*$ and $a_1<\tilde{a}_1(a)$ [compare (13a)], one obtains

$$M(z)=\left[\frac{2a}{\frac{1}{2}b+\sqrt{\bar{R}}\,\sinh(2\sqrt{a}z+\bar{S})}\right]^{1/2}, \tag{35a}$$

with

$$\bar{R}=\tfrac{4}{3}c(a-a^*)\,, \tag{35b}$$

$$\bar{S}=\text{arcsinh}\left[\frac{1}{\sqrt{\bar{R}}}\left[-\frac{1}{2}b+\frac{2a}{M_1^2}\right]\right]. \tag{35c}$$

At E^+, this function again has the characteristic shape shown in Fig. 3(d).

VI. SURFACE FREE ENERGY

Phase transitions in semi-infinite systems show up as singularities in the surface free energy f_s. In Landau theory, this quantity is given by (7) [when the equilibrium profile $M(z)$ is inserted]. Again very similar results are found for $[x,y]=[3,4]$ and for $[x,y]=[4,6]$. Therefore we will only consider the first case in this section while the latter case is discussed in Appendix A.

In the low-temperature regime with $a<a^*$, one finds

$$f_s=\tfrac{1}{2}a_1M_1^2+I(M_1,M_B)+J(M_1,M_B)\ , \qquad (36a)$$

with

$$I(M_1,M_B)=\frac{Q}{2c^2}\left[c-\frac{Q}{M_B-M_1}\right]a_1M_1+\frac{2}{3c}a_1^3\left[\frac{M_1}{M_B-M_1}\right]^3+\frac{Q^2}{2c^2}P^{1/2}-\frac{2}{3c}P^{3/2}\ , \qquad (36b)$$

$$J(M_1,M_B)=2^{-3/2}c^{-5/2}QR\ln\left[\frac{\bar{A}+(\bar{A}^2+R)^{1/2}}{-Q+(Q^2+R)^{1/2}}\right] \qquad (36c)$$

where the parameters P,Q,R are given by (22b)-(22d) and the parameter $\bar{A}$ is given by (26b). At the transitions O_2 and $\bar{s}$, the surface free energy f_s develops a nonanalytic part. As $a=a^*$ is approached with $a_1>(a^*)^{1/2}$, one finds the asymptotic behavior,

$$I(M_1,M_B)=\sigma^*-\tfrac{1}{2}a_1M_1^2+O(|\delta a|)\ , \qquad (37a)$$

$$J(M_1,M_B)=\frac{(a^*)^{1/2}}{c}|\delta a|\beta_1|\ln|\delta a||+O(|\delta a|)\ , \qquad (37b)$$

where β_1 in (37b) is the surface exponent (15b) and

$$\sigma^*=\frac{1}{3c}a^{*3/2} \qquad (38)$$

in (37a) is the surface tension of the interface in an infinite system with boundary conditions $M(-\infty)=0$ and $M(\infty)=M_B^*$. If (37a) and (37b) is inserted into (36a), one finds

$$f_s=\sigma^*+\frac{(a^*)^{1/2}}{c}|\delta a|\beta_1|\ln|\delta a||+O(|\delta a|) \qquad (39)$$

at the transitions O_2 and $\bar{s}$. In addition to the leading nonanalytic ln term in (39), there are nonanalytic corrections: at O_2, there are terms proportional to $M_1^3\propto|\delta a|^{3/2}$, and at $\bar{s}$ terms proportional to $M_1^4\propto|\delta a|^{4/3}$ arise. Note that (39) gives $f_s=\sigma^*$ for $a=a^*-0$. In contrast, $f_s=0$ at the other side of the phase boundary with $a=a^*+0$. This implies that there is still an interface for $a=a^*-0$ which is, however, an infinite distance apart from the free surface.

In the high-temperature regime with $a>a^*$, (7) leads to $f_s=0$ for $a_1>\tilde{a}_1(a)$. For $a_1<\tilde{a}_1(a)$, one finds

$$f_s=\tfrac{1}{2}a_1M_1^2+\bar{I}(M_1)+\bar{J}(M_1)\ , \qquad (40a)$$

with

$$\bar{I}(M_1)=\frac{b}{3}(M_1-M_B^*)|a_1|+\frac{2}{3c}|a_1|^3+\frac{1}{c}a^*\sqrt{a}-\tfrac{2}{3}a^{*3/2}\ , \qquad (40b)$$

$$\bar{J}(M_1)=\frac{(a^*)^{1/2}}{c}\delta a\ln\left[\frac{(c/2)^{1/2}(M_1-M_B^*)+|a_1|}{a^{1/2}-a^{*1/2}}\right]. \qquad (40c)$$

As the transition E^+ is approached from above, (40a) has the asymptotic behavior,

$$f_s=f_s^*+\sigma^*+\frac{(a^*)^{1/2}}{c}\delta a|\ln(\delta a)|+O(\delta a)\ , \qquad (41a)$$

where σ^* is the surface tension (38) and

$$f_s^*=-\frac{1}{3c}[|a_1|^3+3(a^*)^{1/2}a_1^2+3a^*|a_1|] \qquad (41b)$$

is the limiting value for f_s at E^-. If f_s in (41a) is set equal to zero, one recovers the expansion (13) for the phase boundary S.

In summary, the surface free energy has a singular part proportional to $|\delta a|\ln|\delta a|$ at the transitions O_2, $\bar{s}$, and E^+. This implies for the surface specific heat,

$$C_s\propto\frac{d^2}{dT^2}f_s\ ,$$

the asymptotic behavior,

$$C_s\propto|T-T^*|^{-\alpha_s}\ , \qquad (42a)$$

with the surface exponent,[25]

$$\alpha_s=1\ \text{ for } O_2,\bar{s},E^+\ . \qquad (42b)$$

VII. DISCUSSION AND OUTLOOK

It has been shown in this paper that several types of phase transitions may occur in a semi-infinite system which undergoes a first-order bulk transition (compare the global phase diagram of Fig. 2). In particular, there are surface-induced disordering transitions denoted by O_2 and $\bar{s}$ where surface quantities show a critical behavior: Surface quantities either go continuously to zero or diverge whereas the bulk quantities behave discontinuously. These transitions occur if the Landau coefficient a_1 in (8b) fulfills the inequality $a_1 \geq (a^*)^{1/2}$. At the transition O_1, i.e., for $-\bar{x}(a^*)^{1/2} < a_1 < (a^*)^{1/2}$ [with $\bar{x}$ given by (13b)], both surface and bulk quantities behave discontinuously. Finally, at E^- and E^+, local quantities such as M_1 are continuous and regular while excess quantities such as M_s [see (31)] or C_s [see (42a)] diverge at E^+.

In order to decide which transition will occur in a real physical system one must express the coordinates of the various phase boundaries in terms of microscopic interaction parameters. Thus one has to investigate appropriate lattice models. From a theoretical point of view, the semi-infinite q-state Potts model is the simplest lattice model which may undergo a first-order bulk transition. In this model, two Potts spins in the surface interact via the coupling constant J_1 while two Potts spins in the bulk interact with the coupling constant J (compare discussion at the end of Sec. II). For $(d,q)=(3,3)$, one finds from mean-field theory[25,44] that $(a,a_1)=[a^*,(a^*)^{1/2}]$ corresponds to the ratio $J_1/J=1.1$ while $(a,a_1)=[a^*,-\bar{x}(a^*)^{1/2}]$ corresponds to the ratio $J_1/J=1.3$. One would expect that $J_1 \lesssim J$ is the rule which implies that the surface-induced disordering transition O_2 could be observed in real samples. Another lattice model of interest which has a first-order bulk transition is an Ising model with competing interactions in a magnetic field. For a face-centered-cubic lattice with antiferromagnetic nearest-neighbor couplings, this model has been used to study the bulk transition of binary alloys such as Cu_3Au.[45] In addition, the corresponding semi-infinite lattice model has been investigated by Monte Carlo methods.[46] The Monte Carlo results for the order-parameter profiles strongly suggest that surface-induced disordering may also occur in such Ising models.

The motivation for the Monte Carlo studies just mentioned came from an experimental result obtained with LEED on Cu_3Au.[47] This binary alloy undergoes an order-disorder transition at $T^*=663$ K which is discontinuous in the bulk. In contrast, it was observed in the LEED experiment that the intensity of the superlattice beam which measures the long-range order parameter in the surface seems to vanish continuously as T^* is approached from below. Unfortunately, there are not enough data points in order to estimate the surface exponent β_1 from this experiment (see Fig. 4 of Ref. 47). Thus more precise measurements of the surface order parameter in Cu_3Au or similar materials would be highly valuable. In this context, new experimental techniques which probe the surface locally such as total reflected x-ray diffraction[48,49] or total reflected neutron beams[50,51] should be very useful.

It has been shown that the critical-surface behavior at the transition O_2 and $\bar{s}$ may be derived from a scaling form for the surface free energy.[27] In this scaling form, two independent surface exponents enter. These two exponents may be taken to be β_1 and β_s which describe the behavior of M_1 and $\hat{l}$, respectively [see (15a) and (28)]. At the transition O_2, the classical values for these exponents are $\beta_1=\frac{1}{2}$ and $\beta_s=0$ (ln). Of course, one must ask how fluctuations which are underestimated in Landau theory will affect these exponents. The relevant fluctuations are expected to be capillary waves which may lead to an interface which is not only delocalized at $T=T^*$, but also rough. Such fluctuations can be investigated via an effective interface model.[52] In $d=2$, this model can be solved exactly.[52] As a result, one recovers the transition O_2 with two independent surface exponents. The values for these exponents are $\beta_1(d=2)=\frac{1}{3}$ and $\beta_s(d=2)=-\frac{1}{3}$. In $d=3$, the interface fluctuations should be less singular than in $d=2$. This leads us to conjecture the following inequalities for the three-dimensional case: $\frac{1}{3} \leq \beta_1(d=3) \leq \frac{1}{2}$ and $-\frac{1}{3} \leq \beta_s(d=3) \leq 0$ (ln).

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APPENDIX A

In this Appendix, some additional formulas for the case $[x,y]=[4,6]$ are collected. First, consider the behavior of the new length scales at O_2, $\bar{s}$, and E^+. For $a \to a^*$, one finds

$$\hat{l}=-\frac{1}{(a^*)^{1/2}}\beta_1 \ln|\delta a|+O(1) \quad \text{for } O_2,\bar{s} \tag{A1a}$$

$$\hat{\hat{l}}=-\frac{1}{2(a^*)^{1/2}}\ln(\delta a)+O(1) \quad \text{for } E^+ \tag{A1b}$$

where the surface exponent β_1 is given by (19). Apart from a factor $\frac{1}{2}$ at E^+, this is identical to the corresponding results for $[x,y]=[3,4]$. [Compare (23) and (30).] The excess quantity M_s may be calculated in closed form at $O_2,\bar{s}$ while at E^+ it is given by an elliptic integral of the first kind. The asymptotic behavior is

$$M_s = \begin{cases} -\frac{2}{\sqrt{b}}\beta_1 \ln|\delta a| & \text{for } O_2,\bar{s} \\ -\frac{1}{\sqrt{b}}\ln(\delta a) & \text{for } E^+ . \end{cases} \tag{A2a}$$

Thus the simple estimate (25) holds again.

Next consider the surface free energy as defined by (7). For $T < T^*$, one obtains

$$f_s = \tfrac{1}{2}a_1 M_1^2 + I(M_1,M_B) + J(M_1,M_B) , \tag{A3a}$$

with

$$I(M_1,M_B) = -\tfrac{1}{2}(M_B^2 + \tfrac{1}{2}R) \times \left[\frac{a_1 M_1^2}{M_B^2 - M_1^2} - M_B\sqrt{2cQ/3} \right] + \frac{3}{4c}M_1 \left[\frac{a_1 M_1}{M_B^2 - M_1^2} \right]^3 - \frac{3}{4c}M_B(2cQ/3)^{3/2} , \tag{A3b}$$

$$J(M_1,M_B) = -\left[\frac{c}{3}\right]^{1/2} (M_B^2 + \tfrac{1}{2}R)R \times \ln \left[\frac{M_1 + (M_1^2 + 2R)^{1/2}}{M_B + (M_B^2 + 2R)^{1/2}} \right] . \tag{A3c}$$

At the transitions O_2 and $\bar{s}$, these functions have the asymptotic form

$$I(M_1,M_B) = \sigma^* - \tfrac{1}{2}a_1 M_1^2 + O(\delta a) , \tag{A4a}$$

$$J(M_1,M_B) = -\tfrac{1}{2}\left[\frac{3}{c}\right]^{1/2} |\delta a| \ln M_1 + O(\delta a) , \tag{A4b}$$

where

$$\sigma^* \equiv \frac{1}{4}\left[\frac{3}{c}\right]^{1/2} a^* \tag{A5}$$

is the surface tension of an interface in the infinite system with boundary conditions $M(-\infty)=0$ and $M(\infty)=M_B^*$. From (A3a), (A4a), and (A4b), the asymptotic behavior of the surface free energy is as follows:

$$f_s = \sigma^* - \frac{1}{2}\left[\frac{3}{c}\right]^{1/2} |\delta a| \beta_1 \ln|\delta a| + O(\delta a) \tag{A6}$$

at $O_2,\bar{s}$. At the multicritical point $\bar{s}$, there are nonanalytical higher-order terms proportional to $M_1^6 \propto |\delta a|^{3/2}$, etc. At the transition O_2, there are no such terms in Landau theory since only even powers of $M_1 \propto |\delta a|^{1/2}$ appear. However, this could be changed as soon as fluctuations are taken into account.

For $T > T^*$, the surface free energy is given by

$$f_s = \tfrac{1}{2}a_1 M_1^2 + \bar{I}(M_1) + \bar{J}(M_1) , \tag{A7a}$$

with

$$\bar{I}(M_1) = \tfrac{1}{4}(M_1^2 - M_B^{*2})|a_1| + \tfrac{1}{4}M_B^{*2}a^{1/2} , \tag{A7b}$$

$$\bar{J}(M_1) = \frac{1}{4}\left[\frac{3}{c}\right]^{1/2} \delta a \times \ln\left[\frac{(c/3)^{1/2}(M_1^2 - M_B^{*2}) + |a_1|}{a^{1/2} - a^{*1/2}} \right] . \tag{A7c}$$

As the transition E^+ is approached, the surface free energy behaves like

$$f_s = f_s^* + \sigma^* - \frac{1}{4}\left[\frac{3}{c}\right]^{1/2} \delta a \ln(\delta a) + O(\delta a) , \tag{A8a}$$

where the surface tension σ^* is given by (A5) and

$$f_s^* = -\frac{1}{2}\left[\frac{3}{c}\right]^{1/2} [(a^*)^{1/2}|a_1| + \tfrac{1}{2}a_1^2] \tag{A8b}$$

is the limiting value for f_s at E^-. From $f_s = 0$ and the expansion (A8a), one obtains the asymptotic form (13) for the phase boundary S

APPENDIX B

In this appendix the singular behavior of the zero-field susceptibilities

$$\chi_{1,1} = \left.\frac{\partial M_1}{\partial h_1}\right|_0 \propto |T - T^*|^{-\gamma_{1,1}} , \tag{B1a}$$

$$\chi_1 = \left.\frac{\partial M_1}{\partial h}\right|_0 \propto |T - T^*|^{-\gamma_1} , \tag{B1b}$$

and

$$\chi_s = \left.\frac{\partial M_s}{\partial h}\right|_0 \propto |T - T^*|^{-\gamma_s} , \tag{B1c}$$

is discussed. M_1 is the surface order parameter (see Sec. IV) and M_s is the surface excess quantity defined in (24) and (31). The surface exponents $\gamma_{1,1}$, γ_1, and γ_s are defined by analogy with the semi-infinite Ising model. The susceptibilities

(B1a)-(B1c) may be derived from

$$\chi(z,z')=\int d^{d-1}\rho G(\vec{\rho};z,z') , \tag{B2}$$

where

$$G(\vec{\rho};z,z')\equiv\langle\phi(\vec{0},z)\phi(\vec{\rho},z')\rangle_c$$

is the two-point correlation function. Within Landau theory, $\chi(z,z')$ satisfies the differential equation,

$$\left[-\frac{d^2}{dz^2}+V(z)\right]\chi(z,z')=\delta(z-z') , \tag{B3a}$$

$$V(z)=\frac{\partial^2 f(M)}{\partial M^2}=\frac{d^3M}{dz^3}\bigg/\frac{dM}{dz} , \tag{B3b}$$

where $M(z)$ is the order-parameter profile (see Sec. V). At $z=0$, one has the boundary condition

$$\frac{d}{dz}\chi(z,z')\bigg|_{z=0}=\frac{\partial^2 f_1(M_1)}{\partial M_1^2}\chi(0,z') . \tag{B4}$$

The general solution to (B3a) and (B4) has the form (compare Ref. 11)

$$\chi(z,z')=\begin{cases} u_1(z)[\bar{B}^{-1}u_1(z')+u_2(z')] , & z>z' \\ [\bar{B}^{-1}u_1(z)+u_2(z)]u_1(z') , & z<z' \end{cases} \tag{B5a}$$

with

$$u_1(z)=\frac{dM(z)}{dz} , \tag{B5b}$$

$$u_2(z)=u_1(z)\int_0^z dx\left[\frac{dM(x)}{dx}\right]^{-2} , \tag{B5c}$$

$$\bar{B}=\frac{\partial^2 f_1}{\partial M^2}\left[\frac{\partial f_1}{\partial M}\right]^2-\frac{\partial f}{\partial M}\frac{\partial f_1}{\partial M}\bigg|_{M=M_1} . \tag{B5d}$$

In terms of $\chi(z,z')$, the susceptibilities (B1a)-(B1c) are given by

$$\chi_{1,1}=\chi(0,0)=\bar{B}^{-1}\left[\frac{\partial f_1(M_1)}{\partial M_1}\right]^2 , \tag{B6}$$

$$\chi_1=\int_0^\infty dz\chi(z,0)=\bar{B}^{-1}\frac{\partial f_1(M_1)}{\partial M_1}(M_B-M_1) , \tag{B7}$$

$$\chi_s=\int_0^\infty dz\left[\chi_B-\int_0^\infty dz'\chi(z,z')\right] , \tag{B8}$$

where χ_B is the bulk susceptibility. We now specialize to model (8). Then the behavior of $\chi_{1,1}$ and χ_1 is easily found to be

$$\chi_{1,1}=\frac{a_1M_1}{(a_1^2-a)M_1+bM_1^{x-1}-cM_1^{y-1}} , \tag{B9}$$

$$\chi_1=\frac{M_B-M_1}{(a_1^2-a)M_1+bM_1^{x-1}-cM_1^{y-1}} . \tag{B10}$$

At the transitions O_2 and $\bar{s}$, the surface order parameter M_1 goes continuously to zero as discussed in Sec. IV. This implies a power-law behavior for χ_1 and $\chi_{1,1}$ as indicated in (B1a) and (B1b) with the surface exponents,[26,27]

$$\gamma_{1,1}=\begin{cases} 0 & \text{for } O_2 \\ \dfrac{x-2}{x} & \text{for } \bar{s} \end{cases} \tag{B11}$$

and

$$\gamma_1=\begin{cases} \frac{1}{2} & \text{for } O_2 \\ \dfrac{x-1}{x} & \text{for } \bar{s} . \end{cases} \tag{B12}$$

It is more difficult to evaluate the susceptibility χ_s Equation (B8) may be brought into the form

$$\chi_s=-\bar{B}^{-1}(M_B-M_1)^2+\int_0^\infty dz\left[\chi_B-\left[\frac{M_B-M(z)}{dM/dz}\right]^2\right]$$
$$-\lim_{L\to\infty}[M(L)-M_B]\int_0^L dz[M_B-M(z)]\left[\frac{dM}{dz}\right]^{-2} . \tag{B13}$$

The second integral is finite at all types of transitions. In contrast, the first integral is singular at the transitions O_2, $\bar{s}$, and E^+. In addition, the first term which involves $1/\bar{B}$ is proportional to $|\delta a|^{-1}$ at (O_2) and $\bar{s}$. As a consequence, one finds

$$\chi_s\propto|T-T^*|^{-1} , \tag{B14}$$

i.e.,

$$\gamma_s=1 \quad \text{for } O_2,\bar{s},E^+ . \tag{B15}$$

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