Critical Surface Phenomena at First-Order Bulk Transitions

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Semi-infinite systems which undergo a first-order bulk transition are considered. A new type of surface phase transition is predicted which has two unexpected features: (1) It exhibits some universal properties since a variety of surface exponents can be defined although there are no bulk exponents; (2) a layer of the disordered phase appears between the free surface and the ordered bulk. The interface between the disordered and the ordered phases becomes delocalized as in the wetting and in the pinning transition.

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Critical behavior at surfaces has been the subject of much recent interest.[1-12] Up to now, both theory and experiments have been devoted to semi-infinite systems which undergo a second-order bulk transition. In this case, the bulk order parameter is proportional to $|T-T_c|^\beta$ as the critical temperature $T=T_c$ is approached from below while the surface order parameter behaves as $|T-T_c|^{\beta_1}$ with $\beta_1 \neq \beta$. This surface critical exponent has been calculated by various methods for the Ising model,[2-5] for the n-vector model,[6-8] and for the two-dimensional q-state Potts-model with $q=3,4$.[9] The exponent β_1 has been measured for the antiferromagnet NiO by low-energy electron diffraction (LEED)[10] and for the ferromagnet Ni by spin-polarized LEED.[11] In this Letter, we consider semi-infinite systems which undergo a *first-order bulk transition.* As a consequence, the bulk order parameter jumps at the transition temperature $T=T^*$. However, it is shown below that *the surface order parameter may nevertheless behave continuously like* $|T-T^*|^{\beta_1}$. *A* variety of surface exponents can be defined which are expected to be universal. This is rather surprising since there are no corresponding bulk exponents. This new type of surface phase transition has an additional unexpected feature: as T^* is approached from below, *a layer of the disordered phase intervenes between the free surface and the ordered bulk.* Thus, an interface appears which separates the disordered surface layer from the ordered phase in the bulk. At $T=T^*$, this interface becomes delocalized as in the wetting[1,13,14] and in the pinning transition.[15-17] This implies a disordered surface layer of macroscopic thickness.

Consider a d-dimensional semi-infinite system with a $(d-1)$-dimensional free surface. The coordinate perpendicular to the surface is denoted by z. As a result of the broken translational invariance, the order parameter M depends on z: $M=M(z)$. The Landau expansion for the free en-

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ergy (per unit area) has the generic form

$$F\{M\} = \int_0^\infty dz\left[\tfrac{1}{2}(dM/dz)^2 + f(M) + \delta(z) f_1(M)\right]. \quad (1)$$

For a system with a bulk tricritical point, the bulk term $f(M)$ is given by the well-known expression

$$f(M) = -HM + \tfrac{1}{2}a(T)M^2 + \tfrac{1}{4}uM^4 + \tfrac{1}{6}vM^6 \quad (2)$$

with $v > 0$. The bulk order parameter follows from $\partial f/\partial M = 0$. For $u > 0$ or $u = 0$ in (2), the bulk transition is critical and tricritical, respectively. The corresponding semi-infinite systems have already been discussed in the literature.[12] Here, we are concerned with $u < 0$ which leads to a first-order bulk transition at $a = a^* = 3u^2/16v$ for $H = 0$ The temperature deviation $T - T^*$ is proportional to $a - a^*$. At $T = T^*$, the bulk order parameter jumps by the amount $(3|u|/4v)^{1/2}$.

In the Landau free energy (1) the additional term $\delta(z) f_1(M)$ mimics the microscopic changes of the interaction parameters near the free surface. If $f_1(M)$ is expanded in powers of M, one obtains

$$f_1(M) = -H_1 M + \tfrac{1}{2}a_1 M^2 \quad (3)$$

up to second order. This form for $f_1(M)$ has been widely used in the context of the semi-infinite Ising model.[1,2,6-8] H_1 is an effective surface field and $1/a_1$ is the so-called extrapolation length which is assumed to be independent of temperature. In the following, a_1 is taken to be positive. In addition, only infinitesimal symmetry breaking fields $H, H_1 \geq 0$ will be considered.[18] In this case, both the bulk and the surface are disordered for $T > T^*$. For an Ising ferromagnet, the corresponding transition is usually called the *ordinary transition.*

From $\delta F/\delta M = 0$, one obtains the differential equation

$$dM/dz = [2f(M) - 2f(M_B)]^{1/2}, \quad (4)$$

where M_B is the bulk order parameter, together with the implicit equation

$$\left(\frac{\partial f_1(M_1)}{\partial M_1}\right)^2 = 2f(M_1) - 2f(M_B) \quad (5)$$

for $M_1 \equiv M(z=0)$ which must be solved in the interval $[0, M_B]$. From (5), one finds the temperature dependence of M_1 for $H = H_1 = 0$ as $T \to T^* - 0$:

$$M_1 \propto \begin{cases} \text{const}, & a_1 < (a^*)^{1/2}, \\ |T - T^*|^{1/4}, & a_1 = (a^*)^{1/2}, \\ |T - T^*|^{1/2}, & a_1 > (a^*)^{1/2}. \end{cases} \quad (6)$$

Thus, two different types of ordinary transitions are obtained, denoted by O_1 and O_2 in Fig. 1. These transitions are separated by the multicritical point $\bar{s}$ as shown in Fig. 1. At the ordinary transition O_1, the surface order parameter M_1 is discontinuous just like the bulk order parameter M_B. However, at the ordinary transition O_2 and at the multicritical point $\bar{s}$, M_1 goes continuously to zero with the surface exponent

$$\beta_1 = \begin{cases} \tfrac{1}{2} & (O_2), \\ \tfrac{1}{4} & (\bar{s}). \end{cases} \quad (7)$$

(Note that Landau theory yields $\beta_1 = 1$ in the case of an Ising ferromagnet.[1,3]) This behavior of M_1 is possible since the order-parameter profile $M(z)$ develops an intrinsic structure as shown schematically in Fig. 2. There is an interface at $z = \hat{l}$ which separates a surface layer of the disordered phase from the ordered phase in the bulk. As $T \to T^* - 0$, this interface becomes delocalized since

$$\hat{l} \propto |\ln M_1| \propto |\ln|T - T^*||. \quad (8)$$

Within Landau theory, such a logarithmic divergence has also been found in the wetting[13] and in the pinning transition.[16] This interface delocalization is due to the possible coexistence of several bulk phases. In the case of the wetting and of the pinning transition, one has coexistence of two ordered phases while in the phase transition considered here the disordered phase coexists with one of the ordered phases.

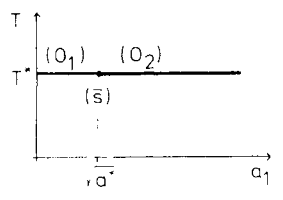

FIG. 1. Phase diagram for $H = H_1 = 0$

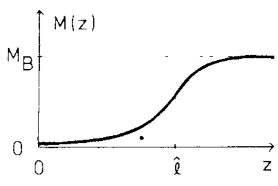

FIG. 2. Order-parameter profile $M(z)$ as O_2 and $\bar{s}$ are approached from $T < T^*$

$M_1 \equiv M(z=0)$ is a local quantity. We may also define a global excess quantity M_s by analogy with the surface magnetization of the semi-infinite Ising model.[1,2] Within Landau theory,

$$M_s = \int_0^\infty dz[M_B - M(z)]. \tag{9}$$

As a result of the diverging length scale $\hat{l}$ at O_2 and $\bar{s}$,

$$M_s \propto |\ln|T - T^*|| \tag{10}$$

at these transitions. Thus, the surface exponent $\beta_s = 0$ at O_2 and $\bar{s}$. The zero-field susceptibilities χ_1, $\chi_{1,1}$, and χ_s also display power-law behavior at O_2 and $\bar{s}$:

$$\chi_1 = \frac{\partial M_1}{\partial H}\bigg|_0 \propto |T - T^*|^{-\gamma_1},$$
$$\chi_{1,1} = \frac{\partial M_1}{\partial H_1}\bigg|_0 \propto |T - T^*|^{-\gamma_{1,1}}, \tag{11}$$
$$\chi_s = \frac{\partial M_s}{\partial H}\bigg|_0 \propto |T - T^*|^{-\gamma_s},$$

with $\gamma_1 = \frac{1}{2}$, $\gamma_{1,1} = 0$, and $\gamma_s = 1$ at the transition O_2 At $\bar{s}$, I obtain $\gamma_1 = \frac{3}{4}$, $\gamma_{1,1} = \frac{1}{2}$, and $\gamma_s = 1$. Both at O_2 and at $\bar{s}$, these surface exponents satisfy the scaling relation

$$2\gamma_1 - \gamma_{1,1} - \gamma_s = 0. \tag{12}$$

The same relation holds for the corresponding surface critical exponents of the semi-infinite Ising model[2] and of the n-vector model.[7]

If $M(z)$ is inserted into the Landau free energy (1), one obtains the surface free energy

$$f_s = f_1(M_1) + \int_0^\infty dz (dM/dz)^2. \tag{13}$$

For $T \to T^* \to 0$ and $H = H_1 = 0$, this quantity has a singular part. To leading order,

$$f_s \propto |T - T^*| \ln|T - T^*| \quad (O_2, \bar{s}). \tag{14}$$

As a consequence, the singular part of the surface specific heat $c_s \propto d^2 f_s/dT^2$ behaves like

$$c_s \propto |T - T^*|^{-\alpha_s} \tag{15}$$

with

$$\alpha_s = 1 \quad (O_2, \bar{s}). \tag{16}$$

It is shown in a forthcoming paper[19] that the singular part of the surface free energy may be put into a scaling form where two independent surface exponents enter. This scaling form implies scaling relations such as (12) for the various surface exponents defined above. Some of these relations are identical with and some are different from the corresponding relations of the semi-infinite Ising model.

I now discuss the effect of higher-order terms in the expression for $f_1(M)$. An appropriate generalization of the polynomial (3) is

$$f_1(M) = -H_1 M + \tfrac{1}{2}a_1 M^2 + \tfrac{1}{4}u_1 M^4 + \tfrac{1}{6}v_1 M^6. \tag{17}$$

with $v_1 > 0$. Two cases have to be distinguished. If the Landau coefficient $u_1 > -|u|/4(a^*)^{1/2}$, all results derived above remain unchanged. If $u_1 < -|u|/4(a^*)^{1/2}$, the phase diagram depicted in Fig. 1 is slightly changed. Instead of the multicritical point $\bar{s}$, a short phase boundary extends into the low-temperature regime with $T < T^*$. Across the additional phase boundary, M_1 is discontinuous while M_B is analytic. However, at the transition O_2, all scaling properties are unaffected by the above generalization of $f_1(M)$

The features of O_2 are also independent of the specific form for the bulk term $f(M)$ in (1). All that is required is a first-order bulk transition. Instead of the polynomial (2), we may consider

$$f(M) = -HM + \tfrac{1}{2}a(T)M^2 - \tfrac{1}{3}bM^3 + \tfrac{1}{4}uM^4 \tag{18}$$

with $b, u > 0$ which arises, for example, in the Landau theory of the q-state Potts model. For $(d,q) = (3,3)$, the discontinuous nature of the bulk transition is now well established.[20-22] From (18) and an expansion of $f_1(M)$ up to fourth order in M, one may derive all previous results for the ordinary transition O_2. Depending on the value of the Landau coefficients in $f_1(M)$, either a multicritical point $\bar{s}$ as in Fig. 1 or a short phase boundary extending into the low-temperature regime is found. At $\bar{s}$, some surface exponents are altered: as a result of the cubic term in (18), $\beta_1 = \frac{1}{3}$, $\beta_s = 0$, $\gamma_1 = \frac{2}{3}$, $\gamma_{1,1} = \frac{1}{3}$, $\gamma_s = 1$, and $\alpha_s = 1$. The scaling relation (12) is again satisfied.

As the temperature T is varied, the physical trajectory of a real sample is given by a straight line parallel to the T axis in the phase diagram of Fig. 1. Thus, in order to decide whether the new ordinary transition O_2 may occur one has to estimate the magnitude of the inverse extrapolation length a_1 in terms of microscopic interaction parameters. As a first step towards this goal, the semi-infinite q-state Potts model on a lattice has been investigated by mean-field theory. For $q \to \infty$, this can be done analytically.[23] For finite q, a "nonlinear dynamics" approach has been used[24] similar to the method described by Pandit and Wortis.[25] Although the phase diagram of the lattice model is more complex the new ordinary transition O_2 is recovered. For $(d,q) = (3,3)$, the transition O_2 occurs for $J_1 \leq 1.1J$, where J_1 is the coupling constant for two Potts spins in the surface and J is the coupling constant for two Potts spins in the bulk. It seems likely that the interaction parameters of real samples fulfill this inequality. In this case, modern experimental techniques like LEED,[10] spin-polarized LEED,[11] or Mössbauer spectroscopy[26] which probe the surface locally may reveal the power-law behavior (6) for materials which undergo a discontinuous bulk transition.

The results reported above have been obtained in the framework of Landau theory which underestimates the effect of fluctuations. There are no critical fluctuations at the phase transitions considered here since the bulk correlation length stays finite at $T = T^*$ but there are fluctuations of the interface, i.e., capillary waves, which should be taken into account. Such interface fluctuations have been studied in the context of the pinning transition where they lead to an interface which becomes not only delocalized but also rough.[15-17] As a consequence, the logarithmic divergence of $\hat{l}$ obtained from Landau theory [compare (8)] is changed to a power-law divergence.[15,17] In the present context, these interface fluctuations also make the various power laws for M_1, M_s, etc., more singular as preliminary calculations for the solid-on-solid model indicate. These effects will be discussed in a forthcoming publication.[27]

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