Surface critical behavior of binary alloys and antiferromagnets: dependence of the universality class on surface orientation

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The surface critical behavior of semi-infinite (a) binary alloys with a continuous order-disorder transition and (b) Ising antiferromagnets in the presence of a magnetic field is considered. In contrast to ferromagnets, the surface universality class of these systems depends on the orientation of the surface with respect to the crystal axes. There is ordinary and extraordinary surface critical behavior for orientations that preserve and break the two-sublattice symmetry, respectively. This is confirmed by transfer-matrix calculations for the two-dimensional antiferromagnet and other evidence.

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A cornerstone of the modern theory of critical phenomena is the idea of distinct universality classes. The bulk universality class to which a particular system belongs is generally determined by a few basic properties, such as the spatial dimension and the symmetries of the order-parameter. In the renormalization-group picture, each universality class corresponds to the basin of attraction of a fixed point in a many-dimensional space of Hamiltonians.

Over the past two decades convincing evidence has emerged for similar universality classes in the surface critical behavior of semi-infinite systems close to the bulk critical point. The surface universality class of a particular system is determined by (i) the bulk universality class and (ii) additional relevant surface properties. In a ferromagnet in zero magnetic field, for example, the strength of the spin couplings near the surface is one of these additional properties. For subcritically, critically, or supercritically enhanced surface interactions, the surface critical behavior is “ordinary”, “special”, or “extraordinary”, respectively. Another relevant surface property is a surface ordering field. The surface critical behavior of a ferromagnet with zero bulk magnetic field and nonzero surface field belongs to the “normal” universality class, independent of the strength of the surface couplings. In both the extraordinary and normal cases there is long-range order near the surface above the bulk critical temperature, and both transitions have the same universal properties. Following common usage we refer to the joint universality class as extraordinary.

Note that the Ising model with \( d \leq 2 \) does not exhibit a “true” extraordinary transition (except for infinite surface couplings), because of the low boundary dimension, but there is a normal transition.

Field-theoretic studies of Ising surface critical behavior begin with the one-component \( \phi^4 \) model with Hamiltonian

\[
H = \int_{\mathbb{R}^d} \left[ \frac{1}{2} (\nabla \phi)^2 + \frac{\gamma_0}{2} \phi^2 + \frac{u_0}{4!} \phi^4 \right] + \int_S \left( \frac{c_0}{2} \phi^2 - h_1 \phi \right)
\]

defined on the half space \( \mathbb{R}^d_+ \equiv \{ (x,y) \in \mathbb{R}^d \mid y \geq 0 \} \) with boundary plane \( S \) at \( y = 0 \). In this model there is ordinary, special, and extraordinary, surface critical behavior at bulk criticality for \( h_1 = 0 \) and \( c_0 > c_{sp} \), \( c_0 = c_{sp} \), and \( c_0 < c_{sp} \) respectively. For \( h_1 \neq 0 \) and arbitrary \( c_0 \) the surface critical behavior is normal.

In this Letter the surface critical behavior of (a) binary alloys with a continuous order-disorder transition and of (b) Ising antiferromagnets in the presence of a magnetic field \( H \) is considered. Our main result is that these systems differ from ferromagnets in an important respect. The surface universality class depends on the orientation of the surface plane with respect to the crystal axes.

That the orientation affects the surface behavior of systems (a), (b) has been recognized by Schmid, who carried out Monte Carlo simulations and mean-field calculations for a lattice model of the A2-B2 order-disorder transition in FeAl, equivalent to an Ising antiferromagnet with a free surface on a bcc lattice. According to Ref., for nonideal bulk stoichiometry (nonzero magnetic field in the equivalent Ising antiferromagnet) the order-parameter symmetry is broken by the (100) surface orientation, and long-range order persists near the surface above the bulk critical temperature \( T_c \). For the (100) surface and ideal stoichiometry or the (110) surface and arbitrary stoichiometry, the symmetry is not broken, and both the bulk and surface order vanish for \( T \geq T_c \).

We agree with these results but question the conclusion that the surface critical behavior at \( T_c \) is ordinary in all of the above cases. We find that the surface universality class depends on the orientation of the surface, with extraordinary surface critical behavior for orientations that break the symmetry of the A and B sublattices (consistent with the renormalization-group relevance of surface ordering fields) and ordinary surface critical behavior for symmetry-preserving orientations. Transfer-matrix calculations in \( d = 2 \) described below confirm these predic-
tions. The predictions are also consistent with an effective field-theoretic Hamiltonian derived from mean-field theory, as outlined below.

As in \( \mathbb{H} \), we consider a simple lattice-gas model in which each site of a bcc lattice is occupied by a particle of type 1 or 2. Nearest-neighbor pairs contribute \( V_{11} \), \( V_{22} \), or \( V_{12} \), depending on the species involved, to the total energy. In the grand canonical ensemble with chemical potentials \( \mu_1, \mu_2 \) the lattice gas is equivalent to an Ising model with Boltzmann factor \( \exp(-\mathcal{H}_{\text{lat}}) \), where

\[
\mathcal{H}_{\text{lat}} = K \sum_{(i,j)} s_i s_j - H \sum_i s_i - H_1 \sum_{i \in \mathcal{S}} s_i.
\]

The bulk and excess surface magnetic fields are given by

\[
H = \frac{1}{2}[(\mu_1 - \mu_2) - \frac{3}{2}\zeta(V_{11} - V_{22})/(kB T)^{-1}]
\]
and

\[
H_1 = \frac{1}{2}(\zeta - \zeta_1)(V_{11} - V_{22})/(kB T)^{-1},
\]

where \( \zeta \) and \( \zeta_1 \) are the coordination numbers of interior and surface sites, respectively. The nearest-neighbor coupling \( K = \frac{1}{2}(V_{11} + V_{22} - 2V_{12})/(kB T)^{-1} \) is assumed to be positive, corresponding to an antiferromagnet, and is the same for surface and interior spins. For \( H/K < \zeta, \ |H + H_1|/K < \zeta_1 \), the system is antiferromagnetically ordered at \( T = 0 \).

The two-dimensional analog of the model is shown in Fig. 1, with the A and B sublattices indicated by filled and empty points.

**FIG. 1.** Symmetry breaking (10) surface (vertical broken line) and symmetry preserving (11) surface (diagonal broken line).

The standard definition of the bulk order parameter of the antiferromagnet in a magnetic field is the difference of the sublattice magnetizations. The conjugate ordering field is a staggered magnetic field. The bulk field \( H \) in (3) is an example of a nonordering field. Increasing \( H \) lowers the critical temperature, at least for weak fields, but does not alter the bulk universality class. As can be seen by redefining the spins on one sublattice with a minus sign, the Ising antiferromagnet is exactly equivalent to an Ising ferromagnet with a nonordering staggered field, irrelevant in the bulk. Thus the same universality classes as in the ferromagnetic Ising model are expected.

The relevance of the surface orientation can be understood from Fig. 1. Suppose that there are \( N \rightarrow \infty \) layers of spins, with free surfaces at the first and \( N \)th layers and periodic boundary conditions in the other direction. For the (11) surface orientation adjacent spins in any layer belong to different sublattices. Both the bulk and surface fields \( H \) and \( H_1 \) in Eq. (3) are nonordering. The Hamiltonian is invariant under a translation of all the spins parallel to the surface by one lattice constant, i.e., under interchange of the A and B lattices. Thus the (11) orientation respects the symmetry of the two sublattices. The order-parameter profile \( \phi_n \), defined as the difference of the sublattice magnetizations in the \( n \)th layer, vanishes for \( T > T_c \) due to symmetry of the sublattices. For \( T < T_c \) there is ordering at the surface driven by the bulk order. Thus ordinary surface critical behavior is expected.

A (10) surface breaks the A-B symmetry of the antiferromagnet, since all the surface spins belong to a particular sublattice. The order-parameter profile is symmetric and antisymmetric about the midpoint of a strip with \( N \) layers for \( N \) odd and even, respectively (see Fig. 3 and Fig. 4 below). This can be understood in terms of the equivalent ferromagnet. The bulk staggered field is constant within a layer but alternates in sign from layer to layer. The fields of magnitude \( |H + H_1| \) on the two surfaces, which are parallel for \( N \) odd and antiparallel for \( N \) even, are ordering fields for this orientation. Under the renormalization group the bulk staggered field is driven to zero, but surface fields with ++ or +− orientations survive. For both the ++ and +− orientation extraordinary critical behavior is expected in the limit \( N \rightarrow \infty \), due to the field-induced order at the surface.

Applying the same reasoning to the three-dimensional analog of the above system (bcc lattice, \( N \rightarrow \infty \) layers, two free surfaces, and periodic boundaries in all other directions), we predict ordinary and extraordinary surface critical behavior for (110) and (100) surfaces, respectively.

The above conclusions also apply if either of the two fields \( H, H_1 \) vanishes. When \( H = H_1 = 0 \) (ideal stoichiometry) the magnetization vanishes on both sublattices for \( T > T_c \). Ordinary critical behavior is expected for arbitrary surface orientations.

We have checked our predictions in \( d = 2 \) with numerical transfer-matrix methods. First the correlation length \( \xi_N(K_c(H), H, H_1) \) parallel to (11) and (10) surfaces of the antiferromagnet (3) defined on a strip of square lattice with \( N \) layers of spins was calculated. Here \( K_c(H) \) is the bulk critical coupling constant, determined as a function of \( H \) with great precision in Ref. [10]. Then the universality class was deduced by comparing \( \pi N^{-1} \xi_N \), with \( \xi_N \) expressed in units of the layer separation, with the known amplitudes

\[
\mathcal{A}^{ab} = \pi \lim_{N \rightarrow \infty} N^{-1} \xi_N^{ab}
\]

for ferromagnetic Ising strips with boundary conditions \( a, b \). The \( \mathcal{A}^{ab} \), which are clearly scale invariant, are universal quantities that depend on the surface universality class. For ferromagnetic Ising strips with ordinary (zero-
Writing the transfer matrix as a product of sparse matrices, we obtained results up to $N = 19$ layers for the (11) orientation and $N = 37$ for the (10) orientation. For more details see Ref. [14].

Representative numerical data are shown in Fig. 2. The quantity $\pi N^{-1} \xi_N$ extrapolates convincingly to the amplitudes $2, 1/2$, and 1 in Eq. (1), in agreement with the surface universality classes predicted above.

The ordinary surface critical behavior expected in system (2) for the (11) orientation and arbitrary values of $H$, $H_1$, and for the (10) orientation in the case $H = H_1 = 0$ (ideal stoichiometry) is confirmed by the transfer-matrix results. The corresponding data in Fig. 2 agree well with $\mathcal{A}_{\text{ord,ord}}^2$. We predict extraordinary surface critical behavior for the (10) orientation with nonvanishing $H$, $H_1$, due to effective ordering surface fields, with $++$ and $--$ orientations for antiferromagnets with odd and even $N$, respectively. This is also confirmed by the transfer-matrix results. The corresponding data in Fig. 2 are in excellent agreement with $\mathcal{A}^{++} = \frac{1}{2}$ for $N$ odd and $\mathcal{A}^{+-} = 1$ for $N$ even. The magnetization and order-parameter profiles in strips of 37 and 36 layers with (10) edges, calculated from the eigenvector with the largest eigenvalue $\lambda_N^{(1)}$, are shown in Fig. 3 and Fig. 4, respectively.

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![Fig. 2. Transfer-matrix results for strips of $N$ layers with (10) and (11) surfaces. For the (10) and (11) orientations, $\tau = 2$ and 1, respectively. The middle two and lower two curves show results for even and odd $N$, respectively.](image1)

![Fig. 3. Magnetization profile of a strip of $N = 37$ layers with (10) surfaces and $H_1 = 0$, $H = 4$, $K = K_c(H)$. Sublattices A and B are indicated by □ and ×, respectively. The order parameter (○) is defined as half the difference of the A and B sublattice magnetizations in adjacent layers.](image2)

![Fig. 4. Same as Fig. 3, but with $N = 36$. Since the surface spins on opposite edges belong to different sublattices, the order-parameter profile is antisymmetric.](image3)

Finally we consider the implications of mean-field theory for the surface universality class. Mean-field theories are, of course, of interest as tractable first approximations. More importantly, one can often infer the appropriate continuum Hamiltonian $\mathcal{H}[\phi]$ for renormalization-group analysis from mean-field theory. The standard pro-
procedure is to begin with mean-field difference equations on a lattice and taking the continuum limit. The appropriate $H[\phi]$ is minimized by the resulting differential equations and boundary conditions, which correspond to the Landau equations $\delta H/\delta \phi = 0$.

As in Ref. [8], we have carried out mean-field studies, but with some differences in approach and conclusions. Here we give a brief summary. The details will be published separately [16,17].

It turns out to be very useful to interpret the rather complex mean-field difference equations as a nonlinear recursive map, an approach pioneered by Pandit and Wortis [13]. For the various surface orientations considered above, the mapping corresponds to discrete Hamiltonian dynamics. The general properties of Hamiltonian flows have been studied extensively [19]. The nonvanishing order parameter profile for $T \geq T_c$ in the case of a symmetry breaking surface orientation can be understood in this context.

Our mean-field equations also provide a convenient starting point for the continuum approximation and, in our opinion, avoid some problematic aspects of earlier work [5]. We are led, apart from irrelevant terms, to the familiar $\phi^4$ Hamiltonian [1] for semi-infinite systems, with a nonzero surface field $h_1$ in the case of symmetry-breaking surface orientations and zero surface field otherwise. The question of surface fields in the continuum Hamiltonian is conveniently analyzed in the framework of Landau-like symmetry arguments [20] and the “method of concentration waves” [21]. As explained in Ref. [17], the bulk amplitudes of all concentration waves that do not share the symmetry of the order parameter vanish in the high-temperature phase. In the presence of a planar boundary translational invariance is lost, and there are some nonzero amplitudes. The effective surface field for symmetry-breaking surface orientations arises from a coupling of the order parameter to nonvanishing concentration waves.

In summary, we have shown that the surface universality class of semi-infinite binary alloys and antiferromagnets depends on the surface orientation, with ordinary and extraordinary behavior for symmetry-preserving and symmetry-breaking orientations, respectively. The underlying mechanism is rather general, and Ising spins are not essential. We expect the orientational dependence to be a common feature of semi-infinite systems with (i) nonordering fields and (ii) second-order phase transitions in which the symmetry of two or more spatially distinct sublattices is spontaneously broken below $T_c$ in the bulk.

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