Surface Critical Exponents in Terms of Bulk Exponents

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The surface exponents associated with critical phenomena in semi-infinite systems are derived exactly in terms of bulk exponents. Results are $\gamma_{1,1}=\nu-1$, $\gamma_1=\nu+(\gamma-1)/2$, $\beta_1=(3-\alpha)/2-\nu$, $\Delta_1=(1-\alpha)/2$, $\eta_\parallel=1/\nu$, and $\eta_\perp=1-(\gamma-1)/2\nu$, where ν, γ, α, etc., are the standard bulk exponents. The bulk-surface crossover exponent is $\varphi_s=1-\nu$. For $\nu>1$ no surface phase can exist.

The problem of critical phenomena in semi-infinite systems has attracted a great deal of attention in recent years.[1-8] New critical exponents associated with the surface have been defined by various authors[3,6-8] and scaling relations among these exponents have been derived.[3-8] These relations suffice to determine all the surface exponents if any one of them is known, but do not fix these exponents absolutely. In this Letter we point out that there is an additional scaling argument by means of which all the surface exponents may be determined in terms of the bulk exponents. Thus *there are no new exponents associated with the surface.*

We take, as a model of the phase transition, a Hamiltonian of the Ginzburg-Landau-Wilson type, containing arbitrary quartic terms (e.g., cubic or other anisotropies may or may not be present). For the sake of simplicity, the quadratic terms in the Hamiltonian will be taken to be of the standard form [see Eq. (8)], although the arguments given here or related ones are sufficient to cover some cases of quadratic anisotropy. The effect of the surface is modeled by the inclusion of an extra "surface" term in the Hamiltonian:

$$H_s=\tfrac{1}{2}c\int d^dx\,\delta(z)\sum_{i=1}^{n}\varphi_i^2(\vec{x}). \tag{1}$$

Here $\varphi_i(\vec{x})$ is the ith Cartesian component of the n-component order parameter. The "surface" perturbation, which destroys translational invariance, is restricted to the plane $z=0$ and the integration in Eq. (1) is over all space, not just the half-space $z\geq 0$. We assume that such a model belongs to the same universality class as a semi-infinite system (except for $\nu>1$, as will be seen later). The parameter c is proportional to the reduction of the local mean-field transition temperature in the surface plane. (For a spin model on a lattice, this corresponds to a reduction of the exchange interaction between spins in the surface layer.) The case $c<0$ corresponds to an enhancement of the local mean-field transition temperature in the surface, and for this case there exists the possibility that the surface will order at a higher temperature than the bulk.[3,5] We restrict ourselves initially to systems for which such ordering does occur whenever $c<0$. Then the transition temperature $T_c(c)$ for the formation of a surface phase is related to c by the crossover exponent[9] φ_s through the relation

$$T_c(c)-T_c(0)\propto|c|^{1/\varphi_s}. \tag{2}$$

Our results are based on the observation that φ_s may be deduced from the scaling properties of H_s, regarded as a perturbation to the bulk Hamiltonian, under a renormalization-group transformation $\mathcal{R}$ in which all lengths are scaled by a factor b, i.e., the transformation $\vec{x}\to b\vec{x}'$. Since

$$\sum_{i=1}^{n}\varphi_i^2(\vec{x})$$

is simply the energy density $e(\vec{x})$, its singular part behaves in the bulk as $\xi^{-(1-\alpha)/\nu}$, where ξ is the correlation length, and so scales as $b^{-(1-\alpha)/\nu}$; thus,

$$e(\vec{x})\to b^{-(1-\alpha)/\nu}e'(\vec{x}'=\vec{x}/b)$$

and

$$\mathcal{R}H_s=c\,b^{d-1-(1-\alpha)/\nu}\int d^dx'\,\delta(z')e'(\vec{x}'=\vec{x}/b). \tag{3}$$

Hence, under the transformation $\mathcal{R}$ the parameter c is rescaled as

$$c'=b^{d-1-(1-\alpha)/\nu}c=b^{(1-\nu)/\nu}c, \tag{4}$$

where we have used the scaling relation $2-\alpha=d\nu$. The eigenvalue[9] associated with c is therefore

$$\lambda_s=(1-\nu)/\nu \tag{5}$$

and the bulk-surface crossover exponent is[9]

$$\varphi_s=\nu\lambda_s=1-\nu. \tag{6}$$

It follows from Eq. (2) that for $\varphi_s<0$, i.e., $\nu>1$, no surface phase can exist. Indeed, the surface Hamiltonian H_s is an irrelevant operator[9] for this

case since c is reduced by each successive application of $\mathcal{R}$. Thus, for $\nu > 1$ and c finite, the system has bulk critical behavior, and therefore belongs to a different universality class from the semi-infinite systems usually considered.[10]

For polymers ($n = 0$), the result Eq. (6) has been derived previously by de Gennes using heuristic arguments.[11] (de Gennes predicted $\varphi_s \simeq \frac{2}{5}$, implicitly using $\nu \simeq \frac{3}{5}$ for polymers.) Indeed, the behavior of polymers at surfaces may provide the most useful application for surface critical phenomena theory.

To determine the critical exponents associated with the surface itself, we consider the local susceptibility $\chi_{1,1}$ which measures the response of a spin in the surface to a magnetic field applied in the surface.[3] $\chi_{1,1}$ may be obtained from the two-point correlation function $G(\vec{\rho}, z, z') = \langle \varphi_i(\vec{\rho}, z) \times \varphi(\vec{0}, z') \rangle$, where $\vec{\rho}$ is the separation of the two points parallel to the surface. Introducing the Fourier transform with respect to $\vec{\rho}$, $\hat{G}(\vec{k}, z, z')$, we have $\chi_{1,1} = \hat{G}(\vec{0}, 0, 0)$. Now $\hat{G}(\vec{k}, z, z')$ is determined from the Hamiltonian H according to

$$\hat{G}(\vec{k}, z, z') = \frac{\int D\varphi\, \varphi_i(\vec{k}, z) \varphi_i(-\vec{k}, z') e^{-H}}{D\varphi e^{-H}}, \tag{7}$$

where $\int D\varphi$ means a functional integration over all order-parameter configurations.

We take H to be of the form $H = H_s + H_0 + H_1$, where H_s is given by Eq. (1),

$$H_0 = \tfrac{1}{2} \sum_{i=1}^{n} \{ r\varphi_i^2 + (\nabla \varphi_i)^2 \} \tag{8}$$

and H_1 contains terms of order φ_i^4 and higher. In Eq. (8), $r \propto (T - T_c^{\mathrm{MF}})/T_c^{\mathrm{MF}}$ where T_c^{MF} is the mean-field transition temperature. It is instructive to consider mean-field theory,[3,5] which consists of neglecting H_1. Then the total Hamiltonian is quadratic in the variables φ_i and one can solve for $\hat{G}(\vec{k}, z, z')$ to obtain[3,5]

$$\hat{G}^{\mathrm{MF}}(\vec{k}, z, z') = \frac{1}{2\kappa} \left\{ \exp(-\kappa |z - z'|) - \frac{c}{c + 2\kappa} \exp[-\kappa(|z| + |z'|)] \right\}, \tag{9}$$

where $\kappa = (r + k^2)^{1/2}$. In Refs. 3 and 5 the expression $c/(c + 2\kappa)$ in Eq. (9) is replaced by $(c - \kappa)/(c + \kappa)$, as these authors employ a half-space rather than the complete space used here. Note that $\hat{G}^{\mathrm{MF}}(\vec{k}, z, z')$ may be written as an expansion in powers of $1/c$:

$$\hat{G}^{\mathrm{MF}}(\vec{k}, z, z') = \frac{1}{2\kappa} \{ \exp(-\kappa |z - z'|) - \exp[-\kappa(|z| + |z'|)] \} + \frac{1}{c} \exp[-\kappa(|z| + |z'|)] + O(c^{-2}). \tag{10}$$

The mean-field expression for the local susceptibility is

$$\chi_{1,1}^{\mathrm{MF}} = (c + 2\sqrt{r})^{-1}. \tag{11}$$

It too has an expansion in powers of $1/c$:

$$\chi_{1,1}^{\mathrm{MF}} = c^{-1} \{ 1 - 2c^{-1}\sqrt{r} + O(rc^{-2}) \}. \tag{12}$$

The critical exponent $\gamma_{1,1}$ is defined by the statement that the most singular part of $\chi_{1,1}$ varies as $r^{-\gamma_{1,1}}$ as $r \to 0$. Thus, $\gamma_{1,1}^{\mathrm{MF}} = -\frac{1}{2}$.

To go beyond mean-field theory, it is necessary to include H_1 in the Hamiltonian. Treating H_1 as a perturbation, we find that the basic elements of the perturbation expansion are the propagators $\hat{G}^{\mathrm{MF}}(\vec{k}, z, z')$. In each order of perturbation theory, $\hat{G}(\vec{k}, z, z')$ may be replaced by the expansion of Eq. (10). This gives, on summing to all orders in the perturbation H_1, a $1/c$ expansion for the exact correlation function $\hat{G}(\vec{k}, z, z')$, and thence a $1/c$ expansion for $\chi_{1,1}$ of the form

$$\chi_{1,1} = c^{-1} \{ 1 - Ac^{-1} t^{-\gamma_{1,1}} + \text{less singular terms} \}, \tag{13}$$

where A is a constant. In Eq. (13), $t \propto (T - T_c)/T_c$, where T_c is the bulk transition temperature. The scaling argument which leads to Eq. (4) implies, however, that the first two terms in Eq. (13) become comparable in magnitude when c is of order $t^{1-\nu}$, whether or not a surface phase exists. Hence we make the identification

$$\gamma_{1,1} = \nu - 1. \tag{14}$$

Equations (6) and (14) are the central results of this paper.

All other surface exponents for $c > 0$ may be deduced from $\gamma_{1,1}$ by means of scaling laws.[3-8] The exponent $\eta_{\parallel}$ describes the decay of correlations parallel to the surface according to $G(\vec{\rho}, z, z') \propto 1/\rho^{d-2+\eta_{\parallel}}$, as $\rho \to \infty$ at fixed z, z'. It is related to $\gamma_{1,1}$ and ν by the scaling law[3] $\gamma_{1,1} = \nu(1 - \eta_{\parallel})$, giving

$$\eta_{\parallel} = 1/\nu. \tag{15}$$

This agrees with exact results for the two-dimensional Ising model,[1] the n-vector model to order $\epsilon = 4 - d$,[4] and the $n = \infty$ limit of the n-vector model for arbitrary d.[12]

The exponent $\eta_\perp$ describes the decay of correlations perpendicular to the surface, $G(\vec{\rho}, z, z') \propto 1/z^{d-2+\eta_\perp}$ for $z \to \infty$ fixed ρ, z'. It satisfies the scaling relation[4] $\eta_\parallel = 2\eta_\perp - \eta$, giving

$$\eta_\perp = 1 - (\gamma - 1)/2\nu, \tag{16}$$

where we have used the bulk scaling law $\gamma = \nu(2 - \eta)$.

The susceptibility χ_1 measures the response of a spin in the surface to a uniform magnetic field.[3,5] Its critical behavior is described by the exponent γ_1, satisfying[3] $\gamma_1 = \nu(2 - \eta_\perp)$, which gives

$$\gamma_1 = \nu + \tfrac{1}{2}(\gamma - 1). \tag{17}$$

The surface gap exponent Δ_1 satisfies[4] $\Delta_1 = \gamma_1 - \nu + \beta$ which gives, using Eq. (17) and the bulk scaling laws,

$$\Delta_1 = \tfrac{1}{2}(1 - \alpha). \tag{18}$$

The surface magnetization exponent β_1 satisfies[8] $2\beta_1 + \gamma_{1,1} = 2 - \alpha - \nu$ giving

$$\beta_1 = \tfrac{1}{2}(3 - \alpha) - \nu = \tfrac{1}{2} + \nu(d - 2)/2, \tag{19}$$

via the scaling law $2 - \alpha = d\nu$. For the Heisenberg model in three dimensions ($\nu \simeq 0.7$) we find $\beta_1 \simeq 0.85$. Measurements of the surface magnetization of NiO using low-energy electron diffraction (LEED) give[13] $\beta_1 \sim 1$, but it is not clear that the data are sufficiently precise to distinguish between an exponent of unity and 0.85. Further experiments, using LEED or the Mössbauer effect, are clearly desirable.

The surface exponent values predicted here are in precise agreement with exact results for the $d = 2$ Ising model,[1] the ϵ expansion to $O(\epsilon)^4$, and the $n = \infty$ limit of the n-vector model.[12] They differ significantly, however, from the exponent values estimated by Binder and Hohenberg on the basis of high-temperature series expansions for the semi-infinite $d = 3$ Ising model.[3] For example, Binder and Hohenberg estimate $\gamma_{1,1}$ to lie in the range $0 \leq \gamma_{1,1} \leq \frac{1}{8}$, corresponding to a diverging local susceptibility $\chi_{1,1}$. Our result $\gamma_{1,1} = \nu - 1 \simeq -0.36$ corresponds to a cusplike singularity in $\chi_{1,1}$. A possible resolution of this discrepancy lies in the observation that the asymptotic form Eq. (13) is restricted to the regime $t^{-\gamma_{1,1}} = t^{1-\nu} \ll c$. In the opposite regime $t^{1-\nu} \gg c$, the critical behavior is dominated, for an infinite system, by the exponents of the bulk transition and, for a semi-infinite system, by those of the "$\lambda = \infty$ transition" defined by Lubensky and Rubin.[5] The mean-field exponent for the latter transition (which corresponds to an enhanced surface exchange not quite strong enough to split off a surface phase[5]) is $\gamma_{1,1}^{MF} = \frac{1}{2}$, corresponding to a diverging susceptibility. We suspect that the series of Binder and Hohenberg are strongly influenced by the existence of this other transition.

Finally, we note that the exponents for the semi-infinite spherical models discussed in the literature[14] differ from those predicted here. These models are, however, somewhat artificial: For bulk systems, the spherical model is equivalent to the $n = \infty$ model in the critical region, but for semi-infinite systems the $n = \infty$ model probably corresponds to a spherical model in which a spherical constraint is applied separately to every layer.[15] As mentioned above, the semi-infinite $n = \infty$ model has been solved exactly[12] and does support the present predictions.

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