Interface delocalization transitions in finite systems

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Interface delocalization transitions are studied for slabs and strips of linear dimension L. For large L, the shift of the transition temperature is found to be proportional to $1/L$. This implies that the continuous behavior predicted for various surface quantities in a semi-infinite geometry becomes weakly discontinuous for large but finite L. The consequences for new experiments and computer simulations on three- and two-dimensional systems are discussed.

Many materials undergo a first-order phase transition. If a symmetry is spontaneously broken at the transition, a disordered phase coexists with several ordered phases. Recently, it was predicted[1,2] that a surface can induce critical phenomena at such transitions. These critical effects include (1) critical behavior of local surface quantities such as the surface order parameter; (2) long-range correlations parallel to the surface; (3) continuous delocalization of the interface between the two (almost) coexisting phases.

The basic physical process behind these critical effects is the following. At the surface, the number of nearest neighbors is smaller than in the bulk. As a consequence, the surface may start to disorder as the first-order transition is approached although the bulk is still in its ordered state. Thus, a layer of the disordered phase intervenes between the surface and the bulk, and the material undergoes a *surface-induced disorder* (SID) transition. SID may occur if the microscopic interaction parameters are comparable or weaker than those in the bulk. On the other hand, if the microscopic surface couplings are sufficiently stronger, the surface may begin to order as the coexistence curve is approached from the other side where the bulk is still disordered. This is a *surface-induced order* (SIO) transition. SIO can also occur in the presence of symmetry-breaking fields which enhance the order at the surface.

In a semi-infinite geometry, the thickness of the surface layer can diverge in a continuous manner. This cannot happen in a real, finite sample. The obvious question is *How far does the disorder intrude into such a finite sample?* The answer to this question [see (11) below] as well as an estimate of finite-size effects in general should prove quite useful in order to guide new experiments and computer simulations for SID. So far, some evidence for this type of transition comes from a low-energy electron diffraction (LEED) experiment on the (100) surface of the binary alloy Cu_3Au, and from a Monte Carlo simulation for an appropriate lattice model of this alloy.[3] Apparently, SID has also been observed in a molecular dynamics study of the melting tansition in a two-dimensional Lennard-Jones system.[4]

SID and SIO are two examples of interface delocalization transitions. They are expected to occur at first-order bulk transitions with a spontaneously broken symmetry as, e.g., (1) in magnetic materials such as metamagnets; (2) in binary alloys; (3) at a Potts-like transition; (4) at the freezing transition of a crystalline solid. Similar delocalization transitions occur in fluids and binary-liquid mixtures at the coexistence curve of two ordered phases. In this context, they are called wetting and drying transitions.[5-16] Although we discuss only SID and SIO, our results can be translated into results for wetting by an appropriate identification of scaling variables.[13,17]

We consider a slab or strip geometry of linear dimension L. The Ginzburg-Landau free-energy functional for a scalar field $\phi(\vec{\rho},z)$ has the generic form

$$F\{\phi\} = \int d^{d-1}\rho \int_0^L dz \left\{ \frac{1}{2}(\vec{\nabla}\phi)^2 + f(\phi) \right.$$
$$\left. + [\delta(z) + \delta(z-L)]f_1(\phi) \right\} . \quad (1)$$

There are two surfaces at $z = 0$ and $z = L$. The $d - 1$ coordinates parallel to these surfaces are denoted by $\vec{\rho}$. In this paper, we discuss (1) with

$$f(\phi) = \frac{1}{2}a\phi^2 - \frac{1}{3}b\phi^3 + \frac{1}{4}c\phi^4 , \quad (2a)$$

$$f_1(\phi) = -h_1\phi + \frac{1}{2}a_1\phi^2 . \quad (2b)$$

The disordered and the ordered bulk phases coexist for $a = a^* = 2b^2/9c$. Thus, the variable $t = (a - a^*)/a^*$ measures the distance from bulk coexistence. In the Potts model, for instance, t is the temperature deviation from the transition temperature.[1,2] The model [(2a) and (2b)] is also equivalent to the Landau-Ginzburg model studied in the context of wetting. If wetting is described in the magnetic language via the equivalence between the lattice gas and the Ising model, the variable t corresponds to the bulk magnetic field of the Ising model.[13,17]

The type of transition which occurs in the semi-infinite system ($L = \infty$) as bulk coexistence ($t = 0$) is approached depends crucially on the values for h_1 and a_1 in (2b). h_1 is a symmetry-breaking field at the surface, and a_1 is related to the ratio of microscopic surface and bulk couplings.[2] For different values of h_1 and a_1, several types of SID and SIO transitions occur as discussed elsewhere.[1,2,18] In the following, we focus attention on the critical and tricritical SID transition for $h_1 = 0$ and $a_1 \geq 1/\xi_d^*$. ξ_d is the correlation length of the disordered phase,[19] and an asterisk indicates that this quantity is considered at coexistence. At these transitions, various surface quantities obey power laws. We concentrate on three such quantities: (1) the local order parameter M_1 in the surface; (2) the correlation length $\xi_{\parallel}$ for correlations parallel to the surface; (3) the thickness l of the disordered layer. For $L = \infty$, mean-field (MF) theory yields the scaling behavior[1,2]

$$M_1^\infty = |t|^{\beta_1}\Omega_1(|t|^{-\Delta_1}h_1) , \quad (3)$$

$$\xi_{\parallel}^\infty = |t|^{-\nu_{\parallel}}\Omega_2(|t|^{-\Delta_1}h_1) , \quad (4)$$

$$l^\infty = -\xi_d^* \ln(M_1^\infty) , \quad (5)$$

where $t \leqslant 0$ and $h_1 \geqslant 0$ are the basic scaling fields.

For finite $L < \infty$, the MF equations for the order parameter $M(z) \equiv \langle \phi(\vec{p}, z) \rangle$ are easily derived from (1). Due to the reflection symmetry of the slab with respect to the plane $z = L/2$, one has the boundary condition $dM/dz|_{z=L/2} = 0$. We have analyzed the MF equations by inspection of the $(M, dM/dz)$ plane, by asymptotic estimates, and by direct numerical integration. Here, we present the main results of this lengthy and somewhat cumbersome analysis. The technical details will be given in a forthcoming paper.[20]

We find that two solutions denoted by $m(z)$ and $M^L(z)$ have to be compared near the SID transitions. The profile $m(z)$ is identically zero for $h_1 = 0$. For small h_1, $m(z)$ is monotonically decreasing for $0 < z < L/2$ with $m(z=0) \propto h_1$. In contrast, the profile $M^L(z)$ is monotonically increasing for $0 < z < L/2$. For small h_1, $M^L(z)$ has two points of inflection at $z = \hat{l}$ and at $z = L - \hat{l}$. For $L \to \infty$, $M^L(z)$ approaches $M^\infty(z)$ which is the equilibrium state of the semi-infinite system for $t < 0$.

The most important effect of L finite is a shift of the bulk coexistence curve from $t = 0$ to $t = t^*(L)$. $t^*(L)$ is determined from the coexistence of the two profiles $m(z)$ and $M^L(z)$, i.e., from

$$\hat{F}\{m(z)\} = \hat{F}\{M^L(z)\} \ , \tag{6}$$

where $\hat{F}$ is the free energy per volume. Equation (6) is implicit for $t = t^*(L)$. In the limit $L/\xi_d \to \infty$, one finds[21]

$$\hat{F}\{m(z)\} = \bar{f}_b + (2/L)[\bar{f}_s + O(e^{-L/\xi_d^*})] \ ,$$

$$\hat{F}\{M^L(z)\} = f_b + (2/L)[f_s + O(e^{-L/\xi_d^*})] \ ,$$

with $\bar{f}_b = \bar{A}t$,[22] $\bar{f}_s \propto h_1^2$, $f_b = At$, and $f_s = \sigma^*$ to leading order in t and h_1. σ^* is the surface tension of a free interface between the disordered and the ordered phases in the infinite system.[2] With $t = t^*(L)$, this leads to the shift

$$t^*(L) = -\frac{2\sigma^*}{(A - \bar{A})L} \ . \tag{7}$$

If the MF expressions for $\bar{A}$, A, and σ^* are inserted, one obtains

$$t^*(L) = -\tfrac{2}{3}\xi_d^*/L \tag{8}$$

for the model [Eqs. (2a) and (2b)]. Thus, $t^*(L)$ is negative at SID. At the SIO transitions, $t^*(L)$ is positive and again proportional to $1/L$.[20]

For the semi-infinite geometry $(L = \infty)$, $\bar{f}_s$ and f_s are the surface free energies for $t > 0$ and $t < 0$, respectively. For $t = h_1 = 0$, $\bar{f}_s = 0$ and $f_s = \sigma^*$ at SID since an interface is present for $t \to 0^-$ but not for $t \to 0^+$.[2] Thus, the discontinuity $f_s(t = 0^-) - f_s(t = 0^+) = \sigma^*$ of the surface free energy at bulk coexistence is responsible for the large temperature shift $\propto 1/L$.

For $t < t^*(L)$, we find in the limit $L \to \infty$,[21]

$$M^L(z = 0) \to M_1^\infty [1 - O(e^{-L/\xi_d})] \ ,$$

$$M^L(z = L/2) \to M_b[1 - O(e^{-L/\xi_d})] \ ,$$

where $M_b \equiv M^\infty$ $(z = \infty)$ is the bulk order parameter. Thus, the profile $M^L(z)$ is indistinguishable from $M^\infty(z)$ for large L apart from exponentially small correction terms. For $t > t^*(L)$, however, the equilibrium state is given by $m(z)$

which is identically zero for $h_1 = 0$. As a consequence, the continuous t dependence found for various surface quantities in the semi-infinite geometry becomes weakly discontinuous for large but finite L. In particular, the quantities discussed in Eqs. (3)–(5) now behave as follows: (1) The surface order parameter $M_1 \equiv M^L(0)$ decreases continuously for $t < t^*(L)$, but at $t^*(L)$ it jumps. For $L \to \infty$ and $h_1 = 0$, this jump is

$$M_1^\infty(t = t^*(L)) \propto L^{-\beta_1} \ . \tag{9}$$

(2) The correlation length $\xi_{\parallel}$ no longer diverges but has the maximum value

$$\xi_{\parallel}^\infty(t = t^*(L)) = L^{\nu_{\parallel}} \bar{\Omega}_2(L^{\Delta_1} h_1) \tag{10}$$

for $L \to \infty$. (3) The thickness $\hat{l}$ of the disordered layer does not diverge either. The maximum value is

$$\hat{l}^\infty(t = t^*(L)) \propto \ln L \tag{11}$$

for $L \to \infty$ and $h_1 = 0$.

The results described so far have been obtained in MF theory which underestimates the effect of interface fluctuations. In space dimension $d = 2, 3$, these fluctuations change some of the MF surface exponents. In addition, they lead to a diverging interface width. However, the MF result (8) for the temperature shift should still hold even in the presence of strong interface fluctuations. All that is required for (8) is a nonvanishing surface tension σ^* for an interface between the disordered and the ordered phase. This implies a discontinuity of the surface free energy at $t = 0$ and, therefore, a shift proportional to $1/L$. Such a shift is also found from the exact solution of an Ising model at zero temperature,[20] and from a mean-field analysis of the q-state Potts model in the $(q \to \infty)$ limit[20] which could also be exact.

In $d = 3$, interface fluctuations do not affect the scaling dimension of t (Refs. 13 and 18) but only of h_1 (Refs. 12, 13, and 15). For $h_1 = 0$, Eqs. (3)–(5) still hold with $\nu_{\parallel} = \tfrac{1}{2}$ and $\beta_1 = 1 - \Delta_1$, where Δ_1 depends on the surface tension in a nonuniversal manner. Thus, we expect that Eqs. (9)–(11) hold in this case. As a consequence, the discontinuity of $M_1 \propto L^{-\beta_1}$ is quite small, and the maximum of $\xi_{\parallel} \propto L^{1/2}$ is quite large for $L \to \infty$. On the other hand, (11) implies that the thickness $\hat{l} \propto \ln L$ of the surface layer is very small in $d = 3$ even for a mocroscopic sample with $L/\xi_d \simeq 10^8$. Note, however, that the scaling dimension of t is changed in $d = 3$ by long-range interactions. For instance, $\hat{l} \propto |t|^{-1/3}$ should hold for wetting transitions in the presence of van der Waals interactions.[7] In this case, the thickness of the surface layer has a maximal value $\propto L^{1/3}$.

In $d = 3$, the interface width $\xi_{\perp}$ as obtained from the effective field theory of Ref. 13 is $\xi_{\perp}^\infty \propto |\ln|t||^{1/2}$ for $L = \infty$ and $h_1 = 0$. For $L < \infty$, the above considerations lead to a maximum value $\xi_{\perp} \propto |\ln(L)|^{1/2}$.

We conclude that the scaling behavior of M_1 and $\xi_{\parallel}$ should be accessible both to experimental studies and computer simulations whereas the divergence of $\hat{l}$ and $\xi_{\perp}$ can hardly be observed in $d = 3$. This conclusion is consistent with the LEED experiment and with the Monte Carlo results of Ref. 3, where the continuous behavior of M_1 has been seen. This behavior of M_1 may also be studied by total-reflected x-rays[23] which have already proved to be a

valuable surface probe in a different context.[24] In addition, it should be possible to measure $\xi_{\parallel}$ by this technique.[25]

Note that there is also a *hysteresis of surface quantities* for finite L due to the presence of a metastable state $M^L(z)$ for t values with $t^*(L) < t < O(e^{-L/\xi_d^*})$ for $L \to \infty$.[20] For this metastable state, the maximum value of $\hat{l}$ in MF is given by $L/4$ instead of $\ln L$. Thus, this metastable state will exaggerate the critical behavior at SID and, therefore, will facilitate its observation in Monte Carlo simulations when coexistence is approached from $t < 0$.

In $d = 2$, interface fluctuations change the scaling dimensions of both t and h_1.[13] However, (3) and (4) still hold with $\beta_1 - \Delta_1 = \frac{1}{3}$ and $\nu_{\parallel} = \frac{2}{3}$, whereas (5) is changed to a power law,

$$\hat{l}^\infty = |t|^{-1/3}\Omega_3(|t|^{-1/3}h_1) \ .$$

In $d = 2$, the interface width $\xi_{\perp}^\infty$ has the same scaling behavior as $\hat{l}^\infty$. Thus, we expect that $\xi_{\parallel} \propto L^{2/3}$, and $\hat{l} \propto \xi_{\perp} \propto L^{1/3}$ at $t = t^*(L)$ and $h_1 = 0$ for large but finite L. These length scales should be observable in computer simulations on two-dimensional systems with a first-order bulk transition. For SID, one should use free boundary conditions in the z direction perpendicular to the surface and periodic boundary conditions in the lateral directions parallel to it. In order to study SIO, one may include symmetry-breaking fields at the surface, or one may even use fixed boundary conditions in the z direction. Periodic boundary conditions in the lateral directions truncate the divergence of $\xi_{\parallel}$ and $\xi_{\perp}$, but are not expected to affect the behavior of $\hat{l}$. Apparently, the length scale $\hat{l}$ has been observed in the computer simulation of Ref. 4 for a Lennard-Jones system. Note that the above analysis may also be applicable to this case with long-range interactions since such interactions should not change the scaling dimension of t for the critical

transition in $d = 2$.[16]

Could SID also be observed experimentally in $d = 2$? Possible candidates are first-order transitions in monolayers of noble gases adsorbed on graphite. These two-dimensional systems consist of crystallites with a typical size $L \sim 1000$ Å.[26] If such systems undergo a SID transition, disordered regions would appear along the boundaries of the crystallites. The fluctuations of the interface between these disordered regions and the ordered "bulk" give a diffuse contribution to x-ray scattering.[20] We find from an effective interface model that the peak amplitude of this diffuse scattering from one crystallite is proportional to $(L\hat{l})^2$, and its linewidth is given by the inverse correlation length $\xi_{\parallel}^{-1}$.

On the other hand, if such a system undergoes a SIO transition, a layer of the ordered phase would appear between the boundaries and the disordered bulk in the middle. The interface fluctuations again lead to a diffuse scattering intensity with a linewidth proportional to $1/\xi_{\perp} \propto 1/\hat{l} \propto t^{1/3}$ with $t > 0$ in this case. Such a behavior may have been observed already in an x-ray scattering experiment for the freezing transition of Xe on graphite.[27] In this experiment, a correlation length $\propto t^{-0.28}$ has been measured which should be compared to $\xi_{\perp} \propto t^{-1/3}$. So far, these correlations have been interpreted either as evidence for a continuous bulk transition,[27] or as an effect due to the exchange of particles from the first to the second adsorption layer at a discontinuous bulk transition.[28] SIO may provide an alternative explanation for these correlations if the bulk transition is discontinuous. The critical effects of SIO occur if the microscopic interaction parameters along the one-dimensional boundaries or edges are such that Xe starts to freeze at these edges.

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[21]In fact, the correction terms are somewhat more complicated since the MF equations do not have a solution for sufficiently small L. This will be discussed in Ref. 20.

[22]Note that $\bar{f}_b = 0$ and thus $\bar{A} = 0$ in MF theory. In general, $\bar{f}_b$ is the analytical continuation of the bulk free energy for $t > 0$ to negative t values. Thus, $A - \bar{A}$ is the latent entropy.

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