SURFACE CRITICAL PHENOMENA AT FIRST-ORDER PHASE TRANSITIONS

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Frequently, first-order phase transitions in solids are characterized by the coexistence of a disordered phase and several ordered phases. Near such a transition, the disordered phase may appear in the surface region of the crystal even though the bulk crystal remains in one of its ordered states. This leads to several critical effects which are characterized by critical exponents. Recent experimental data on order-disorder transitions and on surface melting seem to agree with the theoretical predictions.

I.   INTRODUCTION

Let us consider a material that undergoes a first-order phase transition. At the transition temperature T^*, several thermodynamic phases may coexist. Frequently, one of those phases is microscopically *disordered* and characterized by the vanishing of some appropriate order parameter. Examples for such first-order transitions are: 1) order-disorder transitions in some binary alloys;[1] 2) antiferromagnetic to para-magnetic transitions in the presence of a magnetic field; 3) some ferroelectric to paraelectric transitions;[2] 4) melting of a crystalline solid.[3] In these examples, the order parameter is: 1) the Bragg-Williams long-range order parameter; 2) the staggered magnetization; 3) the polarization; 4) the Fourier component of the density with the lattice periodicity.

At the transition temperature T^*, the bulk order parameter, any M_b, jumps from a finite value which characterizes one of the ordered phases to the value $M_b = 0$ associated with the disordered phase, see Figure 1a. Such a discontinuous behavior does not seem to be particularly interesting. However, much more interesting effects can occur if one studies *surface*[4] rather than bulk phenomena. It turns out that the surface of a crystal can induce *critical phenomena* at a first-order phase transition.[5-11] In particular, the *surface order parameter,* say M_1, may *go continuously to zero,* see Figure 1b. Thus, surface critical exponents can be defined and studied even though there are no bulk exponents.

The basic physical mechanism behind these critical effects is the following. At the crystal surface, the number of nearest neighbors of a given atom or molecule is smaller than in the bulk. As a consequence, the surface may start to disorder as the transition temperature T^* of the first-order phase transition is approached even though the bulk crystal remains in its ordered state. Then, a layer of the disordered phase *intervenes* between the surface and the bulk, and the material may undergo a *surface-induced disorder transition.*[5-8]
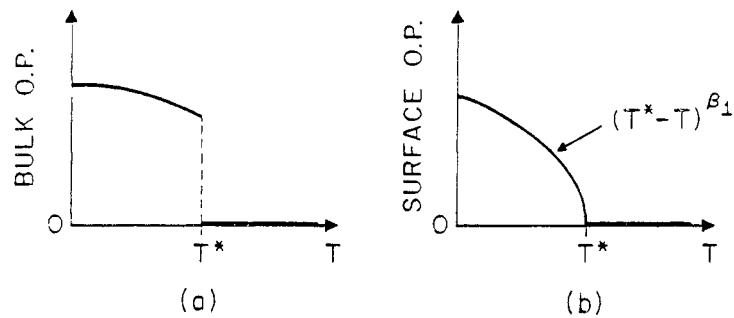
FIGURE 1   (a) Bulk order parameter, and (b) surface order parameter M_1 as a function of temperature T The first-order phase transition occurs at $T = T^*$

The layer of the disordered phase is shown schematically in Figure 2. In this figure, the vacuum[12] surrounding the crystal has been included as a distinct thermodynamic phase. In this way, it becomes apparent that the disordered layer is contained in the interface between the ordered phase and the vacuum. Thus if one introduces three interfacial tensions Σ_{od}, Σ_{dv} and Σ_{ov} where the subscripts o, d, and v stand for ordered phase, disordered phase, and vacuum, the phenomenon of surface-induced disorder implies that $\Sigma_{ov} = \Sigma_{od} + \Sigma_{dv}$. In a fluid context, this equality is known as *Antonow's rule,*[13] and the corresponding three phase equilibrium as *wetting.*[14-16] Thus, one might say that, at a surface-induced disorder transition, the disordered phase wets the interface between the ordered phase and the vacuum.

At such a transition, several critical effects occur: 1) the surface order parameter goes continuously to zero, see Figure 1b and Section II; 2) the thickness of the disordered layer diverges, see Section III; 3) if the interface between the disordered layer and the ordered bulk is rough, the interfacial correlation length also diverges, see Sections IV and V. The surface critical exponents which characterize these critical effects are expected to be *universal,* i.e., they should depend only on the spatial dimensionality d, and, to some degree, on the nature of the underlying microscopic forces. For the sake of clarity, only *three-dimensional* systems will be discussed here. Furthermore, it will be assumed in Sections II-V that the critical
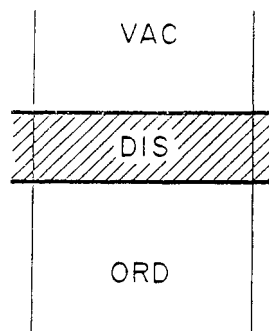

FIGURE 2   A layer of the disordered (DIS) phase appears in the surface region of the crystal while the bulk crystal remains in one of its ordered (ORD) phases Thus, the disordered phase wets the interface between the ordered bulk phase and the vacuum (VAC) surrounding the crystal

behavior is governed by *short-range* forces. The influence of *long-range* forces is discussed in Appendix A.

This paper is basically a review of previous work.[5-11] However, it also contains new results on critical surface scattering (Section V), on the possible influence of long-range forces (Appendix A), and on the critical exponent β_1 for the surface order parameter (Appendix B). Apart from Appendix B, all technical details have been omitted while the physics of the phenomena involved has been emphasized. The reader who is interested in a review of the more formal aspects of this work is referred to Reference 5.

II.   SURFACE ORDER PARAMETER

Let us consider a crystal with an ideal surface free of impurities, and let us focus on the most typical case where the interactions between the atoms in the surface are comparable to or smaller than those between the atoms in the bulk.[17-19] It is also assumed here that the field conjugate to the order parameter vanishes both in the surface region and in the bulk.[20] This is automatically fulfilled for order-disorder transitions in binary alloys and for antiferromagnetic to paramagnetic transitions since, in these cases, the conjugate field in a staggered field which is zero for real physical systems. For ferroelectrics, on the other hand, the conjugate field is the electric field. Therefore, only ferroelectrics in zero electric field are considered here.[21]

If the microscopic interactions have the properties just described, one expects that the surface order parameter, say M_1, is smaller than the bulk order parameter M_b since a surface atom has fewer nearest neighbors than a bulk atom. Thus, one would also expect that the jump of M_1 at the temperature T^* of the first-order phase transition is smaller than the jump of M_b. It turns out, however, that the surface order parameter M_1 does *not* jump at all for the range of interactions considered here, but *goes,* instead, *continuously to zero* as[6-8]

$$M_1 \propto t^{\beta_1} \quad \text{with } \beta_1 > 0 \tag{1}$$

for $T \to T^*$ where $t \equiv (T^* - T)/T^*$ is the reduced temperature. The value for the surface critical exponent β_1 is discussed in Section III below. Note that this exponent was originally introduced for the critical behavior of the surface order parameter M_1 at a *second-order* phase transition in the bulk,[4,22] i.e., when the bulk order parameter M_b goes continuously to zero as well. Here, the same notation is used even though the bulk phase transition is *first* order.

The rather different behavior of the bulk and the surface order parameter is shown schematically in Figure 1. It seems that such behavior has already been observed at the first-order phase transition of the binary alloy Cu_3Au. This alloy undergoes a discontinuous order-disorder transition in the bulk at the temperature $T^* = 663$ K. In contrast, low energy electron diffraction experiments[23,24] indicate that the intensity of the superlattice reflection which measures the long-range order parameter M_1 at the surface vanishes continuously as $T \to T^*$. Thus, this alloy appears to undergo a surface-induced disorder transition.[8,25]

III.   DISORDERED (OR "DEAD") SURFACE LAYER

A simple explanation for the surprising behavior (1) of the surface order parameter can be obtained in the following way. Let us decompose the semi-infinite crystal into a 2-dimensional surface region and a 3-dimensional bulk domain. If there were no couplings between those two systems, the surface would become disordered at its own transition temperature T_1^*. If the couplings within the surface are comparable to those within the bulk, mean field theory leads to the estimate $T_1^* \simeq \frac{2}{3} T^*$. Thus, for the temperature interval $T_1^* < T < T^*$, the surface would be disordered while the bulk is ordered. Of course, this picture is too crude since the surface *is* coupled to the bulk. Its influence on the surface may be thought of as an effective field exerted on the surface atoms. The continuous behavior (1) of the surface order parameter M_1 would now be understandable if this effective field became weaker and weaker as $T \to T^*$. This is, in fact, what happens for the systems considered here since a whole *layer of the disordered phase*[26] *intrudes between the surface and the ordered bulk.* Thus, the growth of the disordered layer as $T \to T^*$ "screens" the effective field which the bulk exerts on the surface.

The thickness $\bar{l}$ of the disordered layer is predicted to diverge as[6-8]

$$\bar{l} \propto \xi_d \ln(1/t), \tag{2}$$

where ξ_d is the correlation length within the disordered phase. Note that ξ_d is a microscopic length here since the bulk phase transition is first order. As mentioned, t is the reduced temperature. More generally, one may define another critical exponent β_s by[7, 8, 22]

$$\bar{l} \propto t^{\beta_s}, \qquad \beta_s \leq 0. \tag{3}$$

The logarithmic behavior (2) corresponds to $\beta_s = 0$; as stated, this is expected for three-dimensional systems governed by short-range forces.

The continuous vanishing (1) of the surface order parameter M_1 and the divergence (2) of the layer thickness $\bar{l}$ are intimately related. This becomes clear if one considers the order parameter profile $M(z)$ which represents the mean value of the order parameter at a distance z from the surface. By definition, the surface is at $z = 0$. Such a profile is shown schematically in Figure 3.[6-8] The mean thickness $\bar{l}$ of the disordered layer can be defined, for instance, by $M(z = \bar{l}) = \frac{1}{2} M_b$ where
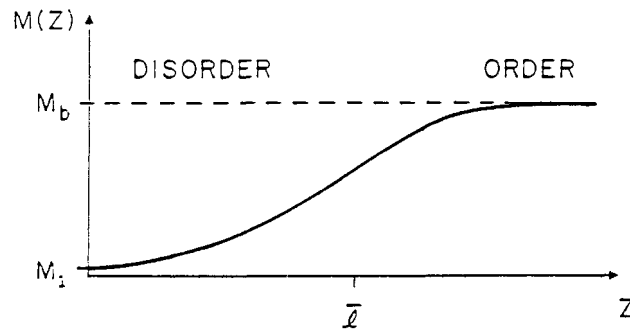

FIGURE 3   Schematic shape of the order-parameter profile $M(z)$ where z measures the distances from the surface The order parameters at the surface and in the bulk are M_1 and M_b respectively

$M_b = M(z = \infty)$ is the order parameter far away from the surface. The order parameter $M_1 = M(z = 0)$, on the other hand, is determined by the *tail* of the order parameter profile near the surface. As $\bar{l}$ goes to infinity, this tail and, therefore, M_1 go continuously to zero.

According to (2), the divergence of the layer thickness $\bar{l}$ is logarithmic when $d = 3$. Such a divergence is obtained for a semi-infinite geometry. In this case, the thickness of the disordered layer can clearly diverge. This cannot happen, however, in a real, finite system: how far does the disorder intrude into such a finite sample? Consider, for example, a slab geometry, and denote the distance between the two surfaces of the slab by L. It is assumed here that the finite crystal consists of a single domain of the ordered phase below T^*. Otherwise, one should regard L as the typical size of such domains. The most important effect of finite L is the shift of the transition temperature.[11, 27] In the limit of large L, one finds[11]

$$T^*(L) \simeq T^* \left[1 - \frac{2\Sigma}{T^* \delta S L} \right], \tag{4}$$

where $T^* \equiv T^*(L = \infty)$. The parameter Σ is the tension of the interface between the ordered and the disordered phase. The entropy $\delta S \equiv S_d - S_o$ is the difference between the entropies of the two phases per unit volume at $T = T^*$. The temperature shift (4) implies that the continuous t-dependence discussed so far is truncated at $T^*(L)$, and, thus, that the transition becomes weakly discontinuous for large but finite L. The surface order parameter M_1, for instance, will have a small discontinuity at $T^*(L)$. Its magnitude is proportional to $L^{-\beta_1}$.[11] From an experimental point of view, this should be a rather small correction. The layer thickness $\bar{l}$, on the other hand, no longer diverges but, rather, grows only up to a maximum value[11] $\propto \ln(L/\xi_d)$. As a consequence, the disordered layer is expected to remain *very thin* as a result of finite size effects.

Thin disordered surface layers have been observed in molecular dynamics studies[28] and in experiments[29] on surface melting. The data obtained in those studies seem to be consistent with a logarithmic divergence of the layer thickness $\bar{l}$ as given by (2). However, long-range van der Waals forces can play an important role as soon as the layer gets sufficiently thick: see Appendix A. As a consequence, a crossover from a logarithmic behavior as in (2) to a power law divergence is to be expected.[30]

Apparently, a disordered surface layer has also been observed for the ferroelectric $NaNO_2$.[31] This material undergoes a first-order phase transition of the order-disorder type at $T^* = 438$ K. Both large, macroscopic crystals and small microcrystals with an average size $L \simeq 50$–200 Å have been investigated by differential thermal analysis. Compared to the bulk measurement, the signal from the microcrystals was found to be broadened towards lower temperatures. This was interpreted as evidence for a surface layer which starts to disorder at about 10 K below T^*[31]

IV. SMOOTH VERSUS ROUGH INTERFACE

Although the disordered layer is expected to be quite thin in real systems, it is instructive to consider the opposite case in which this layer is, in fact, very thick. In such a situation, the *interface* between the disordered surface layer and the ordered

bulk, see Figure 2, is no longer affected by the presence of the surface. Such an interface can be either *smooth* or *rough*.[32] If the interface is smooth, it will be essentially flat on length scales large compared to the lattice spacing. If it is rough, it will make arbitrarily large excursions from its average position. A smooth interface "feels" the underlying lattice structure; a rough interface does not.

For 3-dimensional systems, one expects a roughening transition[32] to occur at some roughening temperature T_R. For $T < T_R$, the interface is smooth while it is rough for $T < T_R$. In order to get an estimate for T_R, let us consider a flat interface with an interfacial tension Σ at low temperatures.[33] The low-energy excitations of such an interface consist of humps with a longitudinal and a transverse dimension comparable to the lattice spacing $\bar{a}$. Such small humps cost an energy $\simeq \bar{a}^2 \Sigma$. A crude estimate for the roughening temperature T_R follows from[34] $k_B T_R \simeq \bar{a}^2 \Sigma$ where k_B is the Boltzmann constant.

Let us now return to the critical surface effects which might occur as one approaches the transition temperature T^* of the first-order phase transition. In order to discuss those effects quantitatively, one has to distinguish two cases:[10,35] 1) $T^* < T_R$ and 2) $T^* > T_R$. If T^* is sufficiently large, the latter case is expected to apply.

First, consider a system with $T^* < T_R$. In such a situation, the interface between the disordered layer and the ordered bulk will always be smooth as $T \to T^*$. This implies that there are no interfacial fluctuations which could affect the growth of the disordered layer. Therefore, the critical exponents β_1 and β_s defined in (1) and (3) should be given correctly by a mean-field theory. This leads to[6-8,36,37]

$$\beta_1 = \tfrac{1}{2}, \tag{5}$$

$$\beta_s = 0(\log) \tag{6}$$

for three-dimensional systems with $T^* < T_R$

If $T^* > T_R$, on the other hand, the interface will fluctuate more and more strongly as the thickness l of the surface layer grows since it is less and less constrained by the surface. These interfacial fluctuations are characterized by two length scales: the interfacial correlation length $\xi_{\parallel}$ and the interfacial roughness $\xi_{\perp}$. As $T \to T^*$, both length scales diverge and one can write[9,10]

$$\xi_{\parallel} \propto t^{-\nu_{\parallel}}, \tag{7}$$

$$\xi_{\perp} \propto t^{-\nu_{\perp}}. \tag{8}$$

For 3-dimensional systems, one has[9,10]

$$\nu_{\parallel} = \tfrac{1}{2}, \tag{9}$$

$$\nu_{\perp} = 0(\sqrt{\log}), \tag{10}$$

i.e., the interfacial roughness diverges as $\xi_{\perp} \propto [\ln(1/|t|)]^{1/2}$ for $d = 3$

The interfacial fluctuations have a rather complicated effect on the critical behavior of the surface order parameter M_1 and on the layer thickness l. The
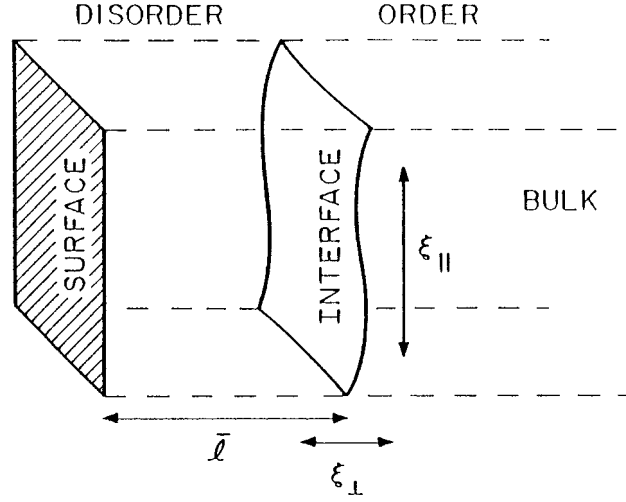
FIGURE 4   The interface which separates the disordered phase near the surface from the ordered phase in the bulk Note that the thickness $\bar{l}$ of the disordered layer has been greatly exaggerated in comparison to the interfacial correlation length $\xi_{\parallel}$

calculation described in Appendix B leads to a continuously varying exponent β_1 with

$$\tfrac{1}{2} < \beta_1 \leq 1 \tag{11}$$

and

$$\beta_s = 0(\log) \tag{12}$$

for $d = 3$ in systems with $T^* > T_R$. Thus, the layer thickness $\bar{l}$ still diverges logarithmically[9] while the exponent β_1 for M_1 is increased by the fluctuations.

The fluctuating interface which separates the disordered layer from the ordered bulk is illustrated in Figure 4. Note that the layer thickness $\bar{l}$ has been greatly exaggerated in this figure since, in general, one has $\bar{l} \ll \xi_{\parallel}$ from (2), (7) and (9). The correlation length $\xi_{\parallel}$ governs the decay of the correlations within the interfacial region. Thus, it would show up in scattering experiments which probe this region. It turns out, however, that $\xi_{\parallel}$ can be observed even *directly at the surface.* This is discussed in the next section.

V.   CRITICAL SURFACE SCATTERING

It is well known that the fluctuations of the order parameter can be investigated by scattering experiments. The diffuse intensity measured in such experiments around the specular beam or around a Bragg reflection contains information about the correlation function of those fluctuations. Let us denote coordinates parallel to the surface by $\mathbf{x} = (x_1, x_2)$, and the perpendicular coordinate by z. In a semi-infinite geometry, the correlation function $C(\mathbf{x} - \mathbf{x}', z, z')$ of two fluctuations at $(\mathbf{x}, z)$ and at $(\mathbf{x}', z')$ may be Fourier transformed with respect to the parallel coordinates to

yield

$$\tilde{C}(\mathbf{q}, z, z') \equiv \int d^2x \, e^{i\mathbf{q} \cdot \mathbf{x}} C(\mathbf{x}, z, z'). \tag{13}$$

This function can be calculated for general values of its arguments within the approximation scheme described on Reference 10.[38]

Let us now consider a scattering experiment such as low energy electron diffraction where the main contribution of the scattering comes from the first few surface layers. In such an experiment, one can essentially observe the correlation function $\tilde{C}(\mathbf{q}, z = 0, z' = 0)$. In general, this function has a somewhat complicated q-dependence. For two regimes of wavenumbers, namely for $q \ll \xi_d^{-1}$ and $q \gtrsim \xi_d^{-1}$, one can obtain separate approximate expressions. For $q \ll \xi_d^{-1}$, one finds[38]

$$\tilde{C}(\mathbf{q}, 0, 0) \simeq \chi_{1,1} \Omega(\xi_\parallel q), \tag{14}$$

where the first factor, $\chi_{1,1} = \tilde{C}(q = 0, 0, 0)$, is a surface susceptibility whose singular part behaves as[7,8,22]

$$\chi_{1,1} \propto |t|^{-\gamma_{1,1}} \tag{15}$$

as $T \to T^*$ with, in fact,[7]

$$\gamma_{1,1} = 1 - 2\beta_1 \tag{16}$$

for three-dimensional systems. From (5) and (11), one obtains $\gamma_{1,1} \leq 0$. Within mean-field theory, there is also an analytic part of $\chi_{1,1}$ which is constant near T^*. Although $\Omega(x)$ in (14) is not a simple Lorentzian,[39] its width is determined by the inverse correlation length $\xi_\parallel^{-1}$ which vanishes as $(T^* - T)^{1/2}$ owing to (7) and (9). On the other hand, for $q \gtrsim \xi_d^{-1}$, the correlation function $\tilde{C}(q, 0, 0)$ is found to decay as $1/q$.[38]

Near a bulk critical point, the amplitude of the diffuse scattering diverges while its width goes to zero. In contrast, the surface critical effects considered here are predicted to lead to a scattering line with an *amplitude* which *remains bounded* near T^* while the *width decreases* as $\xi_\parallel^{-1} \propto (T^* - T)^{1/2}$. Apparently, such an unusual behavior of the diffuse scattering has been observed in the recent low-energy electron diffraction experiment on the binary alloy Cu_3Au by McRae and Malic.[24] In fact, the width of the diffuse scattering observed in this experiment has been found to decrease as $(T^* - T)^{1/2}$, in agreement with the theoretical prediction (9) for the critical exponent $\nu_\parallel$.

APPENDIX A: SHORT-RANGE VERSUS LONG-RANGE FORCES

As mentioned in the introduction, it has been assumed in Sections II-V that the critical surface behavior is governed by *short-range* forces. In this case, a disordered layer of thickness l has an excess free energy per unit area or an effective interfacial potential[9]

$$V(l) = c\Sigma \exp(-2l/\xi_d) + T^*\delta St l. \qquad (A.1)$$

The parameter Σ is the tension of the interface between the ordered and the disordered phase. The entropy $\delta S \equiv S_d - S_o$ is the difference between the entropies of the two phases per unit volume at $T = T^*$. The constant c is of $O(1)$.[40] As before, ξ_d is the correlation length within the disordered phase and $t \equiv (T^* - T)/T^*$

The first and the second term of (A.1) are repulsive and attractive in the sense that they favor a large and a small value for the layer thickness l, respectively. The exponential l-dependence of the repulsive term is due to the exponential tails of the order parameter profile $M(z)$ discussed in Section III.[41] If the interface is rough, i.e., if $T^* > T_R$ as discussed in Section IV, the overall entropy loss of the interface due to the presence of the surface leads to an additional repulsive term with a similar l-dependence.[42]

Short-range forces lead to the exponential term in (A.1) which favors the formation of a disordered layer. It is well known, on the other hand, that any pair of neutral or ionized particles interacts via long-range, induced-dipole–induced-dipole or *van der Waals forces*.[43] If one ignores retardation effects, the potential energy for a pair of particles decays as $-\varepsilon(r/\lambda)^{-6}$ for large separations r between the particles. The parameters ε and λ are the energy and length scale of this pair potential. This leads to an additional term $V_{LR}(l)$ in the excess free energy (A.1). For large l, one has[43,44]

$$V_{LR}(l) = Wl^{-2}, \qquad (A.2)$$

where W is the so-called Hamaker constant. In the present context, an estimate for this constant is given by[45]

$$W = \frac{\pi}{12}\varepsilon\lambda^6(\rho_o - \rho_d)\rho_d, \qquad (A.3)$$

where the parameters ρ_o and ρ_d are the particle number densities of the ordered and the disordered phase, respectively. From (A.3), one concludes that the sign of W should be determined by the sign of $(\rho_o - \rho_d)$.

Let us consider the case $\rho_o > \rho_d$, i.e., $W > 0$. First of all, it seems plausible to assume that the r^{-6} tails of the interparticle forces do not significantly affect a thin layer up to a thickness, say, $l/\xi_d \lesssim 3$. This implies that the term (A.2) can be ignored for reduced temperatures $t \gtrsim t_{SR}$ with $t_{SR} \simeq 5 \times 10^{-3}\Sigma/(T^*\delta S\xi_d)$. For $t < t_{SR}$, on the other hand, short-range forces alone would lead to $l/\xi_d > 3$, and the term $V_{LR}(l)$ might become important. Two extreme cases have to be distinguished. For a large Hamaker constant $W \gtrsim W_>$, with $W_> \simeq 10^{-1}\xi_d^2\Sigma$, the long-range

forces will come into play as soon as $l/\xi_d \simeq 3$. On the other hand, the Hamaker constant might be so small that the term (A.2) will *never* play any role for a single-phase domain of finite size. This happens for $W \lesssim W_<$ with

$$W_< \equiv f(L/\xi_d)\xi_d^2 \Sigma \qquad (A.4)$$

and

$$f(x) \equiv \tfrac{1}{8}\ln^3(x)/x, \qquad (A.5)$$

where L is the linear dimension of the single-phase domains.

A rough estimate of the Hamaker constant (A.3) is

$$W \simeq \varepsilon(\rho_o/\rho_d - 1) \qquad (A.6)$$

since $\lambda^3\rho_d$ can be taken to be of $O(1)$. Thus, if the particle densities of the two phases are sufficiently close, W may be much smaller than ε and one could get into the regime with $W < W_<$ where the van der Waals forces can be neglected.

For a solid phase, the particle number density ρ is roughly equal to $1/\bar{a}^3$ where $\bar{a}$ is the lattice parameter. Thus, the Hamaker constant (A.6) is large if the lattice parameters of the two phases are sufficiently different. In such a situation, elastic forces can also be important.[46] Such forces tend to truncate the divergence of the layer thickness. This has been found for models with both short-range[47, 48] and with long-range interactions.[49] Therefore, in order to investigate the critical effect described in this paper experimentally, one should look for physical systems where the lattice parameter of the ordered and the disordered phase are as similar as possible. In such systems, both van der Waals and elastic forces may be neglected.

APPENDIX B: THE CRITICAL EXPONENT β_1

The effect of interfacial fluctuations on the surface critical behavior described in Sections II and III can be studied in the framework of effective interface models. The free energy functional or effective Hamiltonian of the interfacial coordinate $l(\mathbf{x})$ has the generic form[44]

$$F\{l\} = \int d^2x \left[\tfrac{1}{2}\tilde{\Sigma}(\nabla l)^2 + V(l)\right]/k_B T. \qquad (B.1)$$

The parameter $\tilde{\Sigma}$ is the interfacial stiffness. In the present context, the interface potential is

$$V(l) = c\Sigma e^{-2l/\xi_d} + T^*\delta St l, \qquad l > 0,$$

$$= \infty, \qquad l < 0, \qquad (B.2)$$

where, in addition to (A.1), a hard wall has been included at $l = 0$ since the interfacial coordinate should be positive. The parameters in (B.2) have been discussed in Appendix A after Equation (A.1).

A variational approximation applied to the model defined by (B.1) and (B.2) leads to the critical singularities[9]

$$\bar{l}/\xi_d = \frac{1}{2}\left[1 + \frac{\tau^2}{2\pi}\right]\ln\frac{1}{t},$$

(B.3)

$$\xi_\perp/\xi_d = \frac{\tau}{2\sqrt{\pi}}\left[\ln\frac{1}{t}\right]^{1/2}$$

(B.4)

for the mean interfacial position $\bar{l}$ and for the interfacial roughness $\xi_\perp$. The parameter

$$\tau \equiv \left(k_B T/\tilde{\Sigma}\right)^{1/2}/\xi_d$$

(B.5)

is dimensionless in $d = 3$. The above behavior for $\bar{l}$ and $\xi_\perp$ is also found if one ignores the hard wall in (B.2) and uses normal ordering to fully renormalize the theory to first order in $V(l)$.[50] Both calculations yield (B.3) and (B.4) for all values of τ.

On the other hand, one may use the scheme described in Reference 51 in order to include the Gaussian fluctuations in a self-consistent way. One then finds that (B.3) and (B.4) are no longer valid for $\tau > \sqrt{2\pi}$. The same conclusion follows from an application of the full renormalization group to first order in $V(l)$ using the potential (B.2) but with the infinite hard wall replaced by one of finite height, i.e., $V(l) = c$ for $l < 0$.[52] In this way, one finds the critical behavior[53,54]

$$\bar{l}/\xi_d = \frac{\tau}{\sqrt{2\pi}}\ln\frac{1}{t},$$

(B.6)

$$\xi_\perp/\xi_d = \frac{\tau}{2\sqrt{\pi}}\left[\ln\frac{1}{t}\right]^{1/2}$$

(B.7)

for $\tau > \sqrt{2\pi}$.

In mean-field theory, the singular part of the surface order parameter is given by[10]

$$M_1 \sim \exp(-\bar{l}/\xi_d)$$

(B.8)

The Gaussian fluctuations change this relation to[53]

$$M_1 \sim \int_0^\infty dl\, e^{-l/\xi_d}\frac{e^{-(l-\bar{l})^2/(2\xi_\perp^2)}}{\sqrt{2\pi}\,\xi_\perp}$$

(B.9)

A change of variables leads to

$$M_1 \sim \exp\left[\frac{1}{2}\left(\frac{\xi_\perp}{\xi_d}\right)^2 - \frac{\bar{l}}{\xi_d}\right]\int_{z_0}^\infty \frac{dz}{\sqrt{\pi}}e^{-z^2}$$

(B.10)

with

$$z_0 \equiv \frac{1}{\sqrt{2}} \left(\frac{\xi_\perp}{\xi_d} - \frac{\bar{l}}{\xi_\perp} \right).$$ (B.11)

If one uses (B.3)-(B.7) in the expression (B.10), one finds $M_1 \sim t^{\beta_1}$ with

$$\beta_1 = \tfrac{1}{2} + \tau^2/8\pi, \quad 0 < \tau < \sqrt{2\pi}$$

$$= \tau/\sqrt{2\pi} - \tau^2/8\pi, \quad \sqrt{2\pi} < \tau < 2\sqrt{2\pi}$$

$$= 1, \quad 2\sqrt{2\pi} < \tau.$$

It is interesting to note that an analogous calculation for the protocritical transition[5] which occurs in the presence of a symmetry breaking field at the surface leads to $\beta_1 = 1$ for all values of τ.

It should be noted that the above calculation is approximate in the sense that all terms which are nonlinear in $V(l)$ have been ignored. Thus, it remains to be proven that the nonlinear terms do not affect the critical behavior dicussed here. These nonlinear terms can be investigated in the framework of Wilson's approximate recursion relation as will be explained elsewhere.[55]

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4. A recent review of surface critical effects is K. Binder, *Phase Transitions and Critical Phenomena,* C. Domb and J. L. Lebowitz, Eds. (Academic Press, New York, 1983) Vol. 8.
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9. R. Lipowsky, D. M. Kroll and R. K. P. Zia, *Phys. Rev. B,* **27,** 4499 (1983)
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11. R. Lipowsky and G. Gompper, *Phys. Rev. B,* **29,** 5213 (1984).
12. In practice, the vacuum may contain some inert gas which does not, however, affect the critical phenomena studied here.
13. J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Clarendon, Oxford, 1982)
14. For wetting phenomena in the context of adsorption, see R. Pandit, M. Schick, and M. Wortis, *Phys. Rev. B,* **26,** 5112 (1982).
15. For wetting phenomena in two-demensional multiphase systems, see M. E. Fisher, *J. Stat. Phys.,* **34,** 667 (1984).
16. A recent review of wetting phenomena in fluids is D. Sullivan and M. M. Telo da Gama, to appear in *Fluid Interfacial Phenomena,* C. A. Croxton, Ed. (Wiley, New York, 1986).
17. The corresponding surface-induced disorder transition has been denoted by (O_2) in References 6-9, and by (C^-) in References 5 and 10. In this case, the so-called extrapolation length λ is smaller than the correlation length within the disordered phase, see Reference 5-11. The concept of the extrapolation length is extensively discussed in Reference 4.
18. It turns out that the cases $\lambda < \xi_d$ and $\lambda = \xi_d$ are critical and tricritical in the sense that they are characterized by two and three relevant scaling fields, respectively, see References 5 and 7. Their scaling properties are, in fact, identical with those at critical and tricritical wetting, see D. M. Kroll and R. Lipowsky, *Phys. Rev. B,* **28,** 6435 (1983).
19. The scaling properties at critical and tricritical wetting are given by H. Nakanishi and M. E. Fisher, *Phys. Rev. Lett.,* **49,** 1565 (1982); see also D. M. Kroll and R. Lipowsky, *Phys. Rev. B,* **28,** 5273 (1983).

20. The vanishing of the conjugate field in the bulk implies that several ordered phases coexist for $T < T^*$

21. In a more realistic model for ferroelectrics, one should include the depolarization field, compare R. Kretschmer and K. Binder, *Phys. Rev. B,* **20,** 1065 (1979).

22. In the context of *second-order* phase transitions in the bulk, critical exponents for surface excess quantities have been introduced by M. E. Fisher, *Critical Phenomena,* M. S. Green, Ed. (Academic Press, London, 1971), and critical exponents for local surface quantities by K. Binder and P. C. Hohenberg, *Phys. Rev. B,* **6,** 3461 (1972). Here, the same notation for the surface critical exponents is used even though the bulk transition is *first* order.

23. V. S. Sundaram, B. Farrell, R. S. Alben and W. D. Robertson, *Phys. Rev. Lett,* **31,** 1136 (1973) and *Surf. Sci,* **46,** 653 (1974).

24. E. G. McRae and R. A. Malic, *Surf. Sci,* **148,** 551 (1984).

25. A continuously vanishing surface order parameter has also been found from mean-field calculations which include the effects of surface segregation, see J. L. Morán-López, F. Mejia-Lira and K. H. Bennemann, *Phys. Rev. Lett,* **54,** 1936 (1985).

26. Strictly speaking, the surface layer is *almost* disordered. Thus, in the case of surface melting, the liquid-like layer is not quite as disordered as a liquid.

27. For wetting phenomena in fluids, the qualitative features of the phase boundary shift have been discussed by H. Nakanishi and M. E. Fisher, *J. Chem. Phys.,* **78,** 3279 (1983).

28. J. Q. Broughton and G. H. Gilmer, *Acta Metall,* **31,** 845 (1983).

29. J. W. M. Frenken and J. F. van der Veen, *Phys. Rev. Lett.,* **54,** 134 (1985).

30. R. Lipowsky (to be published).

31. P. Marquardt and H. Gleiter, *Phys. Rev. Lett.,* **48,** 1423 (1982).

32. See J. D. Weeks, *Ordering in Strongly Fluctuating Condensed Matter Systems,* T. Riste, Ed (Plenum, 1980).

33 The interfacial *stiffness* $\tilde{\Sigma}$ which governs the long-wavelength excitations is infinite for $T < T_R$, see M. E. Fisher and D. S. Fisher, *Phys. Rev. B,* **25,** 3192 (1982).

34. This estimate cannot be used for $d = 2$ since, in this case, the excitation energy does not depend on the horizontal dimension of the hump For $d = 2$, in fact, one has $T_R = 0$

35 In the context of adsorption, this distinction has been emphasized in Reference 14

36 These values for β_1 and β_s can be obtained either from Landau theory or from mean-field theory applied to lattice models. In the latter case, both M_1 and $\bar{l}$ exhibit a series of small jumps as a function of t so that the exponents describe only, say, the envelope function: see Reference 6.

37. For the tricritical case $\lambda = \xi_d$, mean-field theory gives $\beta_1 = \frac{1}{3}$ and $\beta_1 = \frac{1}{4}$ for systems with and without a cubic term in the free energy, see Reference 7 where the tricritical transition is denoted by $(\bar{s})$

38 R. Lipowsky (unpublished).

39 For $q \ll 1/\xi_d$, one finds $\Omega(x) \simeq (1 + \mu x^2)/(1 + x^2)$ with $\mu \equiv 1 - \lambda/\xi_d$ where λ is the extrapolation length.

40. Within Landau theory, $c = \xi_d(\xi_d - \lambda)/[\lambda(\xi_d + \xi_o)]$ where ξ_d, ξ_o, and λ are the correlation lengths within the disordered and within the ordered phase, and the extrapolation length, respectively.

41 An exponential term $\exp(-l/\xi)$ was first obtained by B. Widom, *J. Chem. Phys.,* **68,** 3878 (1978) for wetting phenomena in fluids.

42. M. E. Fisher and D. S. Fisher, as cited in Reference 33.

43 I. E. Dzyaloshinskii, E. M. Lifshitz and L. P. Pitaevskii, *Adv. Phys.,* **10,** 165 (1961).

44 R. Lipowsky, *Phys. Rev. B,* **32,** 1731 (1985).

45 This expression can be obtained from Equation (2.23) of Reference 44 if one replaces ρ_V, ρ_L and ρ_s by ρ_o, ρ_d and 0, respectively.

46 See H. Wagner, *Hydrogen in Metals,* G. Alefeld and J. Völkl, Eds. (Springer, 1978)

47. J. Lajzerowisz, *Ferroelectrics,* **35,** 219 (1981).

48. W. Speth, University of Munich preprint (1985).

49. The interplay between long-range van der Waals forces and elastic forces has been studied for wetting by solid films by D. A. Huse, *Phys. Rev B,* **29,** 6985 (1984); F. T. Gittes and M. Schick, *Phys. Rev. B,* 30, 209 (1984).

50 D. M. Kroll and R. Lipowsky, *Phys. Rev. B,* **26,** 5289 (1982).

51. E. Brezin, B. Halperin and S. Leibler, *Phys. Rev. Lett.,* **50,** 1387 (1983). Their parameter ω is related to the parameter τ used in References 5 and 9 by $\omega = \tau^2/4\pi$.

52. D. S. Fisher and D. A. Huse, *Phys. Rev. B,* **32,** 247 (1985).

53 R. Lipowsky (unpublished).

54 The same behavior is found for the protocritical transition, i.e., for the interface potential $V(l) = A \exp(-l/\xi) + tl$ when $\tau > 2\sqrt{2\pi}$, see Reference 52 and R. Lipowsky, *Phys. Rev. Lett.,* **52,** 1429 (1984).

55. R. Lipowsky and M. E. Fisher (to be published).