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Surface Induced Disordering at First-Order Bulk Transitions

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Semi-infinite systems may undergo surface induced disordering transitions. These transitions exhibit both critical surface behaviour and interface delocalization phenomena. As a consequence, various surface exponents can be defined although there are no bulk exponents. It is shown that the corresponding power laws can be derived from a scaling form for the surface free energy where two independent surface exponents Δ_1 and α_s enter. In addition, global phase diagrams with finite symmetry breaking fields are also briefly discussed.

1. Introduction

Considerable effort has been devoted to the critical behaviour at surfaces [1]. Two types of surface phenomena have been firmly established so far: *1)* as the critical temperature T_c of a second-order bulk transition is approached, various surface quantities obey power laws and thus several surface exponents may be defined [1-3]. *2)* in Ising-like systems, there may occur interface delocalization transitions at the coexistence curve of the two ordered phases below T_c [4-7]. Recently, it has been found [8, 9] that *both types of surface phenomena may occur simultaneously as the transition temperature T^* of a first-order bulk transition is approached.* Power laws for various surface quantities have been derived, and thus several surface exponents have been defined although there are no bulk exponents. For example, as T^* is approached from below the order parameter M_1 at the surface goes continuously to zero: $M_1 \propto |T-T^*|^{\beta_1}$ with $\beta_1>0$ while the order parameter M_B in the bulk jumps by a finite amount. At the same time, a layer of the disordered phase appears between the surface and the ordered bulk. Thus, there is an interface which seperates the disordered layer from the ordered bulk. This interface becomes delocalized since its distance $\hat{l}$ from the surface behaves as $\hat{l} \propto |T-T^*|^{\beta_s}$ with $\beta_s \leqq 0$. (Mean field theory yields a logarithmic divergence for $\hat{l}$ and thus, $\beta_s=0$ (log) is the classical value.) Therefore, this transition may be called a surface induced disordering (SID) transition. Apparently, this transition has been already observed in the binary alloy Cu_3Au [10].

In this paper, some results contained in my previous letter [8] are discussed in more detail. After the definition of the Landau free energy (Sect. 2), an enlarged phase diagram for SID is described in Sect. 3. As a result, one can distinguish three different types of (continuous) SID transitions denoted by (O_2), $(\bar{s})$, and $(\bar{\bar{s}}\bar{p})$. In addition, a discontinuous surface transition denoted by (S') can also occur. This transition is discussed in Sect. 4. The scaling phenomenology which has been referred to in [8] is presented in Sect. 5. The surface free energy is put into a scaling form. As a consequence, scaling relations are obtained: all surface exponents may be expressed in terms of two independent ones. In Sect. 6, the global phase diagram with finite symmetry breaking fields is briefly discussed. It is found that SID is the intersection point of several phase boundaries. Finally, some experimental aspects and related work on interface fluctuations is mentioned in Sect. 7.

2. Landau Free Energy

Consider a d-dimensional semi-infinite system with a $(d-1)$-dimensional free surface. The coordinate perpendicular to the surface is denoted by z. Due to the broken translational invariance, the order parameter M which is taken to be a scalar depends on z. For large z, $M(z)$ approaches the value of the order parameter in the bulk denoted by M_B. The Landau free energy functional is given by [8, 9]

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

The bulk term $f(M)$ which yields a first-order bulk transition has the generic form

$$f(M)=-hM+\tfrac{1}{2}aM^2-\frac{1}{x}bM^x+\frac{1}{y}cM^y \quad (2)$$

with b, $c>0$. The surface term $f_1(M)$ is taken to be of the same form:

$$f_1(M)=-h_1M+\tfrac{1}{2}a_1M^2-\frac{1}{x}b_1M^x+\frac{1}{y}c_1M^y \quad (3)$$

with b_1, $c_1\geqq 0$. As usual, the dominant temperature dependence is assumend to be contained in the Landau coefficient $a=a(T)$. The transition temperature T^* corresponds to $a=a^*$. The remaining coefficients are taken to be temperature-independent. The coefficient a_1 which enters the surface term $f_1(M)$ is related to the relative strength of microscopic interaction parameters in the bulk and in the surface [9]. In the following, the case $a_1>0$ will be discussed which implies that the coupling constants in the surface are equal or smaller than those in the bulk. (The phase diagram with $a_1<0$ and infinitesimal symmetry breaking fields h and h_1 is discussed in [9].)

For systems with a scalar order parameter which allow a cubic invariant the integer exponents in (2) and (3) are given by $(x, y)=(3, 4)$. In this case, the first-order transition occurs at $a=a^*=2b^2/(9c)$. Note that this model allows only for the coexistence of the disordered phase with one ordered phase. In general, there may be several ordered phases if some symmetry is spontaneously broken at the bulk transition. For instance, q ordered phases occur in the q-state Potts-model. If one wants to study the coexistence of several such ordered phases, an order parameter with several components may be required. For instance, the Potts order parameter has $(q-1)$ components [14, 15]. However, as long as one studies the coexistence of the disordered phase with one of the ordered phases, the model (1)-(3) with $(x, y)=(3, 4)$ and the scalar order parameter M should be applicable [11-13]. In this case, M should be considered as an appropriate "projection" of the many-component order parameter. As a consequence, the values for the symmetry breaking fields h, h_1 have to be restricted to $h, h_1\geqq 0$ in this case.

If the disordered phase can coexist with two ordered phases and if the cubic term is not allowed because of symmetry one is lead to consider the model (1)-(3) with $(x, y)=(4, 6)$. All systems which have a bulk tricitical point belong to this class. The tricritical bulk transition occurs for $a=b=0$ in (2). The corresponding semi-infinite case has been investigated by Landau theory [16, 17] and by field-theoretic renormalization [17]. Here, I am concerned with $a, b>0$ in (2) where the bulk transition is first-order.

In the following sections, the semi-infinite model defined by (1)-(3) is analyzed in the framework of Landau (or mean-field) theory. This method has been described previously in some detail [e.g. 1, 9]. Therefore, only the results will be discussed while the details of the derivation will be omitted.

3. Surface Induced Disordering (SID)

In this section, model (1)-(3) is considered with infinitesimal symmetry breaking fields h, $h_1\geqq 0$, and with b_1, $c_1>0$ in (3). In this case, the SID transitions occur when the transition temperature $T=T^*$ is approached from below and the Landau-coefficients a_1 and b_1 fulfill certain constraints. The corresponding phase boundaries in the (T, a_1, b_1)-space are shown in Fig. 1. There is a special SID transition $(\bar{s}\bar{p})$ which occurs at the point with coordinates $(T, a_1, b_1)=(T^*, \sqrt{a^*}, \bar{b}_1)$ with [8]

$$\bar{b}_1=\begin{cases}\sqrt{\dfrac{c}{2}} & (3,4)\\[2ex] \sqrt{\dfrac{c}{3}} & (4,6)\end{cases} \quad (4)$$

This point is the endpoint of the line of SID transitions $(\bar{s})$ given by $(T^*, \sqrt{a^*}, b_1)$ with $b_1<\bar{b}_1$. For

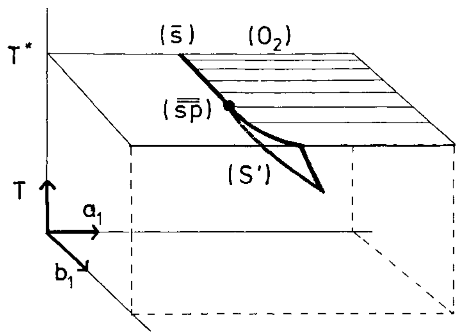

Fig. 1. Phase diagram in the (T, a_1, b_1)-space. T is the temperature, and a_1, b_1 are the Landau coefficients in (3). In addition to the discontinuous surface transition (S'), there are three types of continuous SID transitions denoted by (O_2) (s), and $(\bar{s}\bar{p})$

$b_1 > \bar{b}_1$, there is a wing of (discontinuous) surface transitions (S') which extends into the low temperature regime with $T < T^*$ [13]. Finally, the SID transition (O_2) occurs when the temperature trajectory hits the shaded area inside the plane $T = T^*$

(O_2), ($\bar{s}$), and ($\bar{s}\bar{p}$) are three different types of SID transitions. As these transitions are approached from the low temperature regime with $h = h_1 = 0$, the order parameter profile $M(z)$ develops an intrinsic structure. There is an interface at $z = \hat{l}$ which seperates a surface layer of the disordered phase from the ordered phase in the bulk [8]. The same behaviour is found at the transition temperature $T = T^*$ for infinitesimal symmetry breaking fields $h, h_1 \to 0^+$. In each case, the interface at $z = \hat{l}$ becomes delocalized. Landau theory yields

$$\hat{l} \propto \begin{cases} |\ln|T - T^*|| & T \to T^* - 0,\ h = h_1 = 0 \\ |\ln(h)| & T = T^*,\ h \to 0^+,\ h_1 = 0 \\ |\ln(h_1)| & T = T^*,\ h = 0,\ h_1 \to 0^+. \end{cases} \quad (5)$$

As the disordered layer grows into the bulk, the local order parameter $M_1 \equiv M(z=0)$ at the surface goes continuously to zero:

$$M_1 \propto \begin{cases} |T - T^*|^{\beta_1} & T \to T^* - 0,\ h = h_1 = 0 \\ h^{1/\delta_1} & T = T^*,\ h \to 0^+,\ h_1 = 0 \\ h_1^{1/\delta_{1,1}} & T = T^*,\ h = 0,\ h_1 \to 0^+. \end{cases} \quad (6)$$

The values of the surface exponents β_1, $1/\delta_1$ and $1/\delta_{1,1}$ as obtained within Landau theory are displayed in Table 1. x and y are the integer exponents which enter in (2) and (3). Note that $\beta_1 = 1/\delta_1$ in all three cases. Similar power laws are well-known for systems with a 2nd order bulk transition [e.g. 1]. The standard example is the ordinary transition (O) of an Ising ferromagnet. The classical values of the corresponding surface exponents have been included in Table 1 for comparison.

Another quantity of interest is

$$M_s := \int_0^\infty dz [M_B - M(z)]. \quad (7)$$

Appropriate surface exponents for this surface excess quantity may be defined as

$$M_s \propto \begin{cases} |T - T^*|^{\beta_s} & T \to T^* - 0,\ h = h_1 = 0 \\ h^{1/\delta_s} & T = T^*,\ h \to 0^+,\ h_1 = 0 \\ h_1^{1/\delta_{s,1}} & T = T^*,\ h = 0,\ h_1 \to 0^+. \end{cases} \quad (8)$$

In Landau theory, one finds that the singular part of M_s is due to the diverging length scale $\hat{l}$: $M_s \propto \hat{l}$ [8]. This relation also holds in the 2-dimensional SOS-models for SID [18, 19]. Thus, I will assume that the singular parts of $\hat{l}$ and M_s are proportional to each other in general. From (5), one finds the classical values $\beta_s = 1/\delta_s = 1/\delta_{s,1} = 0$ (log) for all three types of transitions. Additional surface exponents may be defined which describe the singular behaviour of the surface free energy and various susceptibilities [8] (compare (15) and (18) below).

Table 1. Classical values for some surface exponents at the transitions (O_2), (s), and ($\bar{s}\bar{p}$) (O) stands for the ordinary transition in an Ising ferromagnet

	β_1	$1/\delta_1$	$1/\delta_{1,1}$
(O_2)	$\frac{1}{2}$	$\frac{1}{2}$	1
($\bar{s}$)	$\frac{1}{x}$	$\frac{1}{x}$	$\frac{1}{x-1}$
($\bar{s}\bar{p}$)	$\frac{1}{y}$	$\frac{1}{y}$	$\frac{1}{y-1}$
(O)	1	$\frac{2}{3}$	1

4. The Discontinuous Surface Transition (S')

As mentioned in the last section, the SID transition ($\bar{s}$) or ($\bar{s}\bar{p}$) occur for $a_1 = \sqrt{a^*}$ and $b_1 \leqq \bar{b}_1$ (see (4)) i.e. provided the coefficient b_1 in the Landau expansion (3) for $f_1(M)$ is not too large. If b_1 becomes larger than $\bar{b}_1$ one finds a wing of discontinuous transitions (S') (see Fig. 1). This wing is attached to the ($T = T^*$)-plane along the curve

$$\hat{a}_1(b_1) = \begin{cases} \sqrt{a^*} + \frac{2}{9}\frac{1}{c_1}(b_1 - \bar{b}_1)^2 & (3, 4) \\ \sqrt{a^*} + \frac{3}{16}\frac{1}{c_1}(b_1 - \bar{b}_1)^2 & (4, 6) \end{cases} \quad (9)$$

for $b_1 \geqq \bar{b}_1$ (see (4)). The coordinates of the other boundary of the wing which extends into the low temperature regime are denoted by $(a, a_1, b_1) = (\hat{\hat{a}}(b_1), \hat{\hat{a}}_1(b_1), b_1)$ with $b_1 > \bar{b}_1$. For general b_1 these coordinates have to be determined numerically. However, in the vicinity of the special SID transition ($\bar{s}\bar{p}$) one can find $\hat{\hat{a}}(b_1)$ and $\hat{\hat{a}}_1(b_1)$ to lowest order in $(b - \bar{b}_1)$ [compare 13]. The result is

$$\hat{\hat{a}}(b_1) = \begin{cases} a^* - \frac{3^4}{2^{12}\sqrt{2}}\frac{c^{3/2}}{b c_1^3}(b - \bar{b}_1)^4 & (3, 4) \\ a^* - \frac{2^5}{3^4\sqrt{3}}\frac{c^{3/2}}{b c_1^2}(b - \bar{b}_1)^3 & (4, 6) \end{cases} \quad (10)$$

and

$$\hat{\hat{a}}_1(b_1) = \begin{cases} \sqrt{a^*} + \frac{9}{32}\frac{1}{c_1}(b_1 - \bar{b}_1)^2 & (3, 4) \\ \sqrt{a^*} + \frac{1}{3}\frac{1}{c_1}(b_1 - \bar{b}_1)^2 & (4, 6) \end{cases} \quad (11)$$

for $b_1 \geqq \bar{b}_1$. Note that $\hat{\hat{a}}_1(b_1) > \hat{a}_1(b_1)$ for $b_1 > \bar{b}_1$ which means that the (S') wing lies in front of the (O_2)-plane. As a consequence, a temperature trajectory parallel to the T-axis in Fig. 1 with $\hat{a}_1(b_1) < a_1 < \hat{\hat{a}}_1(b_1)$ hits both the (S')-wing and the (O_2)-plane.

Along the (S')-wing, the order parameter M_1 in the surface jumps by a finite amount while the bulk order parameter M_B varies smoothly. This behaviour may be understood by the following qualitative argument [12, 13]. As far as the local behaviour of the surface order is concerned, the influence of the d-dimensional bulk on the $(d-1)$-dimensional surface may be replaced by a temperature-dependent, symmetry-breaking field $h_{\text{eff}}(T)$. Obviously, $h_{\text{eff}}(T)=0$ if the bulk is disordered (i.e. $T>T^*$) and $h_{\text{eff}}(T)>0$ if the bulk is ordered (i.e. $T<T^*$). If the $(d-1)$ dimensional surface undergoes a first-order transition for $h_{\text{eff}}=0$, it will also undergo a transition for finite h_{eff} (as long as h_{eff} is not too large). This is just the behaviour at (S'): the surface order parameter M_1 undergoes a first-order transition in the effective field $h_{\text{eff}}(T)$ of the ordered bulk for $T<T^*$

Such a discontinuous behaviour of M_1 has also been found in the mean field theory of the q-state Potts model [12] if one performs the continuum limit of the mean-field equations [13]. (Note that the transition (S') has been denoted by (S_2) in [12]). However, one has to be careful especially in the 3-dimensional case. This is due to the fact that the 2-dimensional q-state Potts model has a continuous transition for $q \leqq 4$ [20, 21]. Thus, the above qualitative argument implies that the transition (S') should not occur for $q \leqq 4$ and $d=3$

5. Scaling Phenomenology for SID*

In this section, the results of Landau theory for the continuous SID transitions (see Sect. 3) are reformulated in terms of scaling fields. One such scaling field denoted by u has to be defined in such a way that $u=0$ corresponds to the bulk coexistence curve where the ordered and the disordered phase coexist. For instance, within Landau theory one has

$$u=(a-a^*)-3ch/b \tag{12}$$

for $(x, y)=(3, 4)$ (see equation (23) below where the expression for the coexistence curve in the (a, h) plane is explicitly given). u has been chosen in such a way that $u<0$ corresponds to the ordered phase. Note that u depends both on the temperature derivation $(a-a^*)$ and on the symmetry breaking field h. The scaling field u governs the aspect of the interface delocalization at SID. In addition to u, the surface field h_1 is also relevant at all three types of SID transitions. This scaling field governs the aspect of critical surface behaviour at SID.

In the semi-infinite Ising ferromagnet where the bulk transition is second-order all power laws describing the critical behaviour at the surface may be derived from a scaling form for the surface free energy f_s [2, 3]. This is also possible in the present case although the bulk transition is first-order. Within Landau theory, the surface free energy f_s for model (1)-(3) may be calculated in closed form [8, 9]. The explicit expressions for $(x, y)=(3, 4)$ and $(4, 6)$ which are rather lengthy are given in [9] and won't be repeated here. In terms of the scaling fields u and h_1, the singular part of these surface free energies may be written as

$$f_s^{(\cdot)}=|u|\,\Omega^{(\cdot)}(|u|^{-\Delta_1} h_1) + \text{const}\cdot|u| \ln\{|u|^{1-\Delta_1}\Psi^{(\cdot)}(|u|^{-\Delta_1} h_1)\} \tag{13}$$

where $(\cdot)$ stands for the various transitions (O_2), $(\bar{s})$, and $(\bar{s}\bar{p})$. The surface exponent Δ_1 is displayed in Table 2. Obviously, it differs for the different transitions. The shape functions behave like

$$\Omega^{(\cdot)}(x) \underset{x\to\infty}{\sim} x^{1/\Delta_1}$$
$$\Psi^{(\cdot)}(x) \underset{x\to\infty}{\sim} x^{1/\Delta_1-1}. \tag{14}$$

There are also crossover effects. Near the transition $(\bar{s})$, the shape functions depend on three relevant scaling fields, e.g.

$$\Omega^{(\bar{s})}=\Omega^{(\bar{s})}(|u|^{-\Delta_1} h_1, |u|^{-\phi_a}\delta a_1)$$

with $\delta a_1 := a_1 - \sqrt{a^*}$. Near $(\bar{s}\bar{p})$, the shape functions depend on four relevant scaling fields, e.g.

$$\Omega^{(\bar{s}\bar{p})}=\Omega^{(\bar{s}\bar{p})}(|u|^{-\Delta_1} h_1, |u|^{-\phi_a}\delta a_1, |u|^{-\phi_b}\delta b_1)$$

with $\delta b_1 := \bar{b}_1 - b_1$ where $\bar{b}_1$ is given by (4). The crossover exponents ϕ_a and ϕ_b are also included in Table 2. (a star $*$ in the table indicates that the corresponding scaling field is irrelevant).

As far as surface exponents are concerned, one may rewrite (13) as

$$f_s^{(\cdot)}=|u|^{2-\alpha_s}\,\Omega^{(\cdot)}(|u|^{-\Delta_1} h_1) \tag{15}$$

* This scaling phenomenology has been referred to in [8] and has been developed independently from the work of Nakanishi and Fisher [22] where the wetting transitions are analyzed in a similiar manner

Table 2. Classical values for the independent surface exponents α_s, Δ_1 and for the crossover exponents ϕ_a, ϕ_b at the transitions (O_2), ($\bar{s}$), and ($\bar{s}\bar{p}$). x and y are the integer exponents which enter in (2) and (3)

	α_s	Δ_1	ϕ_a	ϕ_b
(O_2)	1	$\frac{1}{2}$	*	*
($\bar{s}$)	1	$\frac{x-1}{x}$	$\frac{x-2}{x}$	*
($\bar{s}\bar{p}$)	1	$\frac{y-1}{y}$	$\frac{y-2}{y}$	$\frac{y-x}{y}$

with $\alpha_s=1$ at all three types of transitions and

$$\Omega^{(\cdot)}(x) \underset{x\to\infty}{\sim} x^{(2-\alpha_s)/\Delta_1}. \tag{15a}$$

This scaling form is similiar to the well-known scaling form for the surface free energy near a second-order bulk transition [2, 3]. However, there are some important differences: *1)* in contrast to the second-order case, only one scaling field depending on the bulk variables h and T enters in (15); *2)* as a consequence, there is no exponent corresponding to the gap exponent Δ of a second-order bulk transition; *3) both α_s and Δ_1 are independent surface exponents.* In contrast, $\alpha_s=(d-1)\nu$ holds in the second-order case where ν describes the divergence of the bulk correlation length. In the present case, there is no bulk exponent ν since the bulk correlation length stays finite at $T=T^*$. The two independent surface exponents α_s and Δ_1 are related to the aspect of interface delocalization and to the aspect of critical surface behaviour respectively.

From the scaling form (15), one may derive scaling relations in the usual way. Thus, the surface exponents which govern the asymptotic behaviour of M_1 are found to be

$$\beta_1=2-\alpha_s-\Delta_1 \tag{16a}$$

$$1/\delta_1=\beta_1 \tag{16b}$$

$$1/\delta_{1,1}=(2-\alpha_s-\Delta_1)/\Delta_1 \tag{16c}$$

and the surface exponents which govern the asymptotic behaviour of the excess quantity M_s are

$$\beta_s=1-\alpha_s \tag{17a}$$

$$1/\delta_s=\beta_s \tag{17b}$$

$$1/\delta_{s,1}=(1-\alpha_s)/\Delta_1. \tag{17c}$$

The surface exponents which describe the power law behaviour of the zero-field susceptibilities [8] $\chi_1=\partial M_1/\partial h|_0$, $\chi_{1,1}=\partial M_1/\partial h_1|_0$, and $\chi_s=\partial M_s/\partial h|_0$ are

$$\gamma_1=\alpha_s+\Delta_1-1 \tag{18a}$$

$$\gamma_{1,1}=\alpha_s+2\Delta_1-2 \tag{18b}$$

$$\gamma_s=\alpha_s. \tag{18c}$$

The scaling relations (16a), (16c), and (18b) also hold for a semi-infinite Ising ferromagnet. However, all remaining scaling relations differ from the corresponding ones in the Ising case. This is due to the fact that the scaling field u in (12) contains both the temperature deviation and the "magnetic" field. Note that a combination of (18a)-(18c) yields $2\gamma_1-\gamma_{1,1}-\gamma_s=0$ as pointed out previously [8]. This relation is also true for the semi-infinite Ising model [3] although the relations (18a) and (18c) do not hold in this case.

In the scaling relations (16)-(18), the space dimension d does not enter explicitly. Thus, these scaling relations should hold beyond Landau theory. This can be shown for $d=2$ in the framework of an effective interface model [19]. On the other hand, one may consider the correlation length $\xi_\parallel$ for fluctuations parallel to the interface with the asymptotic behaviour

$$\xi_\parallel \propto |u|^{-\nu_\parallel}, \quad h_1=0. \tag{19}$$

This correlation length is related to the singular part of the surface free energy via the hyperscaling relation [compare 7]

$$\xi_\parallel^{-(d-1)} \propto f_s. \tag{20}$$

From (20) and (15), one obtains

$$\xi_\parallel^{(\cdot)}=|u|^{-\nu_\parallel}\bar{\Omega}^{(\cdot)}(|u|^{-\Delta_1}h_1) \tag{21}$$

with

$$(d-1)\nu_\parallel=2-\alpha_s \tag{21a}$$

and

$$\bar{\Omega}^{(\cdot)}(x) \underset{x\to\infty}{\sim} x^{-\nu_\parallel/\Delta_1}. \tag{21b}$$

In Landau theory, one finds $\alpha_s=1$ and $\nu_\parallel=1/2$ [19]. Thus, (21a) holds in Landau theory for $d=3$ which is the upper critical dimension for SID [19]. (21a) can also be checked explicitly for $d=2$ where $\alpha_s=4/3$ and $\nu_\parallel=2/3$

The length scale $\xi_\parallel$ governs the fluctuations parallel to the interface. There is another length scale

$$\xi_\perp \propto |u|^{-\nu_\perp}, \quad h_1=0 \tag{22}$$

which measures the thickness of the interface and thus the fluctuations perpendicular to the interface. In Landau theory, $\xi_\perp$ stays finite at the SID transition i.e. $\nu_\perp=0$. In $d=2$, the effective interface model yields $\nu_\perp=1/3$. Thus, $\nu_\perp=|d-3|\nu_\parallel/2$ holds in both cases.

6. Global Phase Diagram with Finite Symmetry Breaking Fields

In this section, the model defined by (1)-(3) is discussed with finite symmetry breaking fields h and h_1, and with $a_1>0$ and $b_1=c_1=0$. First, consider $(x, y)=(3, 4)$. In this case, the bulk coexistence curve $h_c(a)$ in the (a, h)-plane is given by

$$h_c(a)=\frac{b}{3c}(a-a^*) \tag{23}$$

with $a^*\leqq a\leqq a^{**}:=b^2/(3c)$. As a consequence, there is a coexistence plane $\mathscr{C}_0$ in the (a, h, h_1)-space which consists of all points with $a^*\leqq a\leqq a^{**}$, $h=h_c(a)$, and arbitrary $h_1\geqq 0$. This plane $\mathscr{C}_0$ is displayed in Fig. 2 where the phase diagram for some special values of a_1, namely for $0<a_1<\sqrt{a^*}$ is shown.

Inside the plane $\mathscr{C}_0$, there is a parabolic curve denoted by (C). This curve touches the upper boundary of $\mathscr{C}_0$ at the point $(\bar{c})$ with coordinates $(a, h, h_1)=(a^{**}, h_c(a^{**}), ba_1/(3c))$. At the points denoted by $(\bar{t})$ in Fig. 2, the curve (C) changes into the line (D) The coexistence plane is divided by (C) and (D) into three distinct parts denoted by I, II, and III in Fig. 2. Interface delocalization occurs at I and II, and along (C) and (D). In addition to $\mathscr{C}_0$, there are two wings attached to the two pieces of (D). One wing extends into the low temperature regime (this one is visible in Fig. 2) whereas the other wing extends into the high temperature regime (this one is not visible in Fig. 2 since it lies behind the plane $\mathscr{C}_0$).

The phase diagram displayed in Fig. 2 looks very similar to one of the phase diagrams discussed recently by Nakanishi and Fisher [22] in the context of the wetting transitions. Indeed, one can show that both phase diagrams can be mapped into each other by an appropriate identification of the Landau coefficients as will be discussed in a separate publication [18]. In particular, it can be shown that the curve (C) in Fig. 2 corresponds to the critical wetting line (denoted by C_w^1 in [22]), the points $(\bar{t})$ to the wetting tricritical points, and the wings to the prewetting transitions.

As mentioned before, Fig. 2 shows the (a, h, h_1) phase diagram for $0<a_1<\sqrt{a^*}$. When the Landau coefficient a_1 is increased, this phase diagram changes in two ways. First, the point $(\bar{c})$ moves to the right. Secondly, the points denoted by $(\bar{t})$ move

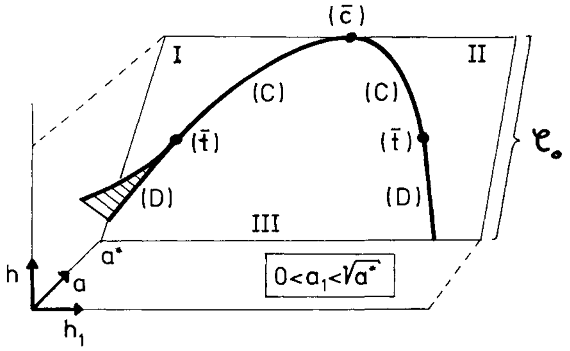

Fig. 2. Phase diagram in the (a, h, h_1)-space for $(x, y)=(3, 4)$ in model (1)-(3) with $0<a_1<\sqrt{a^*}$. $a-a^*$ is proportional to the temperature deviation $T-T^*$. $\mathscr{C}_0$ is the coexistence plane where the ordered and the disordered phase coexist. The various phase boundaries inside $\mathscr{C}_0$ are explained in the text

downwards. At $a_1=\sqrt{a^*}$, they touch the $(h=0)$ plane: their coordinates are $(a, h, h_1)=(a^*, 0, 0)$ and $(a^*, 0, 2b\sqrt{a^*}/(3c))$. As a consequence, the two pieces of (D) together with the wings disappear for $a_1\geqq\sqrt{a^*}$ from the relevant part of the phase diagram with $h\geqq 0$

The SID transitions (O_2) and $(\bar{s})$ which have been discussed in Sect. 3) and Sect. 5) correspond to the single point $(a^*, 0, 0)$ in the (a, h, h_1)-phase diagram: $(\bar{s})$ occurs for $a_1=\sqrt{a^*}$ whereas (O_2) occurs for $a_1>\sqrt{a^*}$. From the above mentioned connection with the wetting problem, it follows that (O_2) belongs to the same universality class as the critical wetting transitions. The same is true for all other points on the curve (C) in Fig. 2. However, the SID point $(a^*, 0, 0)$ is distinguished from all other points on (C) by the property that it belongs to several such phase boundaries. This is due to the fact that there are several distinct ordered phases for $a<a^*$ (i.e. several ground states). For instance, consider the 3-state Potts model for $d=3$. The corresponding mean-field phase diagram for the bulk problem is well known [14]. (It is now generally believed that these results of mean-field theory are correct in $d=3$ [21, 23, 24].) In this case, there are three different ordered phases. Each of these ordered phases may coexist with the disordered phase. As a consequence, there are three pairs of symmetry breaking fields h^α and h_1^α with $\alpha=1, 2, 3$ which favour one of the ordered phases respectively. For each pair h^α, h_1^α, one has a phase diagram like the one depicted in Fig. 2 (Note, however, that only two of the pairs h^α, h_1^α are linearly independent). These three phase diagrams are embedded in a 5-dimensional space and glued together along the a-axis. Thus, the SID point $(a^*, 0, 0)$ is the intersection point of three phase

boundaries similiar to (C) for the 3-state Potts modell in $d=3$

This property of the SID point can be more easily displayed for systems where only two ordered phases can coexist with the disordered phase. Such systems are described by model (1)-(3) with $(x, y)=(4, 6)$. In this case, the bulk term $f(M)$ in the Landau free energy has three local minima denoted by M_-, M_d and M_+ with $M_- < M_d < M_+$. Thus, there are three bulk coexistence curves $\mathscr{C}_{+-}$, $\mathscr{C}_{d+}$, and $\mathscr{C}_{d-}$ as shown in the (a, h)-plane in Fig. 3 [25]. As a consequence, there are three coexistence surfaces in the (a, h, h_1)-phase diagram for the semi-infinite system which I also denote by $\mathscr{C}_{+-}$, $\mathscr{C}_{d+}$, and $\mathscr{C}_{d-}$. Inside these coexistence surfaces, one finds again phase boundaries similiar to the phase boundary of Fig. 2 for $(x, y)=(3, 4)$. For the plane $\mathscr{C}_{+-}$, these phase boundaries are denoted by (C_{+-}) $(\bar{t}_{+-})$, and (D_{+-}) (see Fig. 4). For $\mathscr{C}_{d+}$ and $\mathscr{C}_{d-}$, the notation is chosen correspondingly.

In Fig. 4, the (a, h, h_1)-phase diagram is shown for a large Landau coefficient $a_1 > 2\sqrt{a^*}$. (For such values of a_1, the phase boundary inside $\mathscr{C}_{d+}$ consists of the curve (C_{d+}) only and the phase boundary inside $\mathscr{C}_{d-}$ consists of the curve (C_{d-}) only.) The geometry of the phase diagram depicted in Fig. 4 can be most easily understood if one first considers the half space $h_1 > 0$. This half space contains the curve (C_{d+}) inside $\mathscr{C}_{d+}$. (C_{d+}) hits the line $(a, h)=(a^*, 0)$ where all three coexistence planes meet in the SID point (O_2) with coordinates $(a^*, 0, 0)$ and in the point denoted by $(\bar{m}_+)$ in Fig. 4. (C_{d+}) also touches the upper rim of $\mathscr{C}_{d+}$ at the point denoted by $(\bar{c}_+)$ in Fig. 4. Inside the coexistence plane $\mathscr{C}_{+-}$ with $h_1 > 0$, there is the curve (C_{+-}) between the points $(\bar{m}_+)$ and $(\bar{t}_{+-})$ (see Fig. 4). At the point $(\bar{t}_{+-})$, the curve (C_{+-}) changes into the curve (D_{+-}). Along (D_{+-}), a wing of discontinuous surface transitions is attached. For $h_1 > 0$, there is no phase boundary inside the coexistence surface $\mathscr{C}_{d-}$ of Fig. 4. So far, the half space with $h_1 > 0$ has been discussed. The other half space with $h_1 < 0$ may be simply obtained by a 180 degree rotation around the a-axis. Obviously, the SID point (O_2) is the intersection point of the phase boundaries (C_{d+}) and (C_{d-})

As mentioned before, Fig. 4 applies for $a_1 > 2\sqrt{a^*}$ For $a_1 = 2\sqrt{a^*}$, the points $(\bar{t}_{+-})$ and $(\bar{m}_+)$ coincide. If a_1 is further decreased, the wings shown in Fig. 4 intersect with the coexistence surfaces $\mathscr{C}_{d+}$ and $\mathscr{C}_{d-}$ However, the topology of the phase diagram in the vicinity of (O_2) does not change until a_1 has been decreased to the value $a_1 = \sqrt{a^*}$. For $a_1 < a^*$, additional wings appear in the vicinity of $(a^*, 0, 0)$ (compare Fig. 2). These phase diagrams will be discussed in more detail in a forthcoming publication.

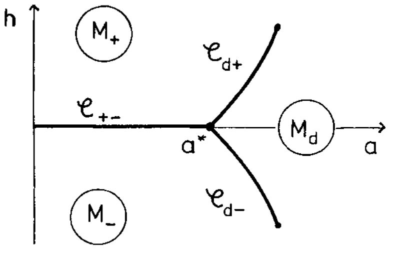

Fig. 3. The three coexistence curves $\mathscr{C}_{+-}$, $\mathscr{C}_{d+}$, and $\mathscr{C}_{d-}$ in the (a, h)-plane for model (1)-(3) with $(x, y)=(4, 6)$ $M_- < M_d < M_+$ denote the bulk order parameters of the three distinct bulk phases which coexist at $(a, h)=(a^*, 0)$

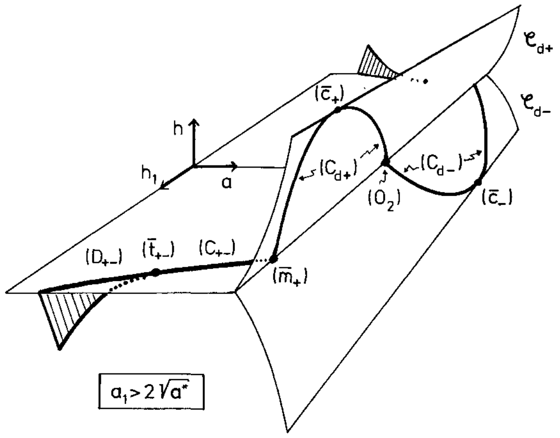

Fig. 4. Phase diagram in the (a, h, h_1)-space for model (1)-(3) with $(x, y)=(4, 6)$. There are three coexistence surfaces $\mathscr{C}_{+-}$, $\mathscr{C}_{d+}$, and $\mathscr{C}_{d-}$. A cross-section through these surfaces with constant h_1 would reproduce Fig. 3. The various phase boundaries within $\mathscr{C}_{+-}$, $\mathscr{C}_{d+}$, and $\mathscr{C}_{d-}$ are explained in the text

7. Discussion and Outlook

It has been shown in this paper that there are three different types of SID transitions denoted by (O_2), $(\bar{s})$, and $(\bar{s}\bar{p})$ (see Fig. 1) which exhibit critical surface behaviour. This surface behaviour is governed by the surface exponent Δ_1 (see Table 2) which depends on the integer exponents x and y in model (1)-(3). At all three types of SID transitions, the interface between the disordered and the ordered phase becomes delocalized in a continuous manner. This interface delocalization is governed by the exponent α_s (see Table 2).

If the Landau coefficient b_1 in (3) is large, the discontinuous surface transition (S') can occur (see Sect. 4). A physical system which is described by constant Landau coefficients b_1 and a_1 with

$$\hat{a}_1(b_1) < a_1 < \hat{\hat{a}}_1(b_1)$$

(compare (9) and (11)) will undergo both the discontinuous transition (S') and the continuous SID transition (O_2). For instance, such a behaviour may occur in the semi-infinite q-state Potts model with $q>4$ in $d=3$ (compare [12] where (S') has been denoted by (S_2)). Note, however, that the mean-field theory for the Potts model on *a lattice* yields additional discontinuous phase boundaries [13].

While the SID transitions ($\bar{s}$) and ($\bar{s}\bar{p}$) occur only for special values of the Landau coefficients a_1 and b_1, the SID transition (O_2) is present for all sufficiently large a_1 (see Fig. 1). As a consequence, (O_2) should most likely be observed in experiments. Recently, new experimental techniques such as low energy electron diffraction (LEED) [26], spin polarized LEED [27], electron capture spectroscopy [28], and total reflected x-ray spectroscopy [29] have been used to investigate surface phenomena. In addition, it has been shown theoretically that total reflected neutron beams may also be used for this purpose [30, 31]. These techniques should now be applied to physical systems which undergo a first-order bulk transition. As a result, one may observe both the continuous behaviour of the surface order parameter $M_1 \propto |T-T^*|^{\beta_1}$ and the divergence of the new length scale $\hat{l} \propto |T-T^*|^{\beta_s}$. Thus, it should be possible to *measure two universal quantities, namely* β_1 *and* β_s *at a first-order transition.* Up to now, there have been no measurements of β_1 or β_s but it seems that the *continuous behaviour of* M_1 *has already been observed* in a LEED experiment on Cu_3Au [10]. This material undergoes an order-disorder transition at $T=T^*=663$ °K which is of first-order in the bulk. In contrast, the experimental results in [10] strongly suggest that the surface order goes continuously to zero at T^* (see Fig. 4 of [10]). Unfortunately, there are not enough data points in order to estimate the exponent β_1 from this experiment. Thus, more precise surface measurements on this material would be highly valuable.

The theoretical work presented in this paper has been obtained in the framework of Landau theory. Of course, Landau theory underestimates the effect of fluctuations. At the SID transitions considered here, there are fluctuations of the interface i.e. capillary waves which will change the classical values of the surface exponents. Such fluctuations may be investigated in the framework of an effective interface model as shown in a seperate publication [19]. In $d=2$, this model can be solved exactly via the transfer matrix method [18, 19]. As a result, the classical values of the surface exponents are indeed changed, e.g. one finds $\beta_1=1/3$ and $\beta_s=-1/3$, but the scaling relations derived in Sect. 5 still hold. In $d=3$, the effective interface model can be investigated by a variational method [19]. As a result, one finds a phase diagram which is even more complex than the phase diagram obtained in Landau theory. In particular, the surface exponent Δ_1 is found to be non-universal: it depends on the surface tension of the interface.

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