Interface delocalization transitions in semi-infinite systems

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The relationship between surface wetting transitions and surface-induced disorder (SID) transitions is studied. The correspondence between the scaling variables at these two types of interface delocalization transitions is derived and the connection between the scaling laws is made explicit. This wetting-SID correspondence is then used to obtain a number of new results. SID transitions are shown to correspond to special points in more general interface delocalization phase diagrams and it is argued that the SID transition is always continuous in $d=2$. Exact results for the surface exponents are obtained in this case. New higher-order multicritical wetting phenomena are also predicted and the scaling behavior of local surface quantities at the wetting transition is discussed in detail.

I. INTRODUCTION

Both surface wetting transitions[1–6] and critical surface-induced-disorder (SID) transitions[7–10] have recently attracted a great deal of attention. The wetting transition was first studied by Cahn in the context of phase separation in binary liquid mixtures below the consulate point.[1] A wetting transition occurs when the angle of contact that the interface between the two coexisting phases makes with a wall or bounding phase becomes zero. For a substrate s in contact with two coexisting phases α and β, the contact angle θ is given by the Young-Duprés relation[11] for the surface tensions γ,

$$\gamma_{\alpha s}-\gamma_{\beta s}=\gamma_{\alpha\beta}\cos\theta \;, \tag{1}$$

where the subscripts designate the phases adjoining the surface or interface. For $\gamma_{\alpha\beta}\geq|\gamma_{\alpha s}-\gamma_{\beta s}|$, (1) has a solution at finite θ (partial wetting). If this inequality is not satisfied, one of the phases completely wets the solid and there is no contact between the solid and the other phase. Assuming phase β wets the surface, (1) then becomes[12,13]

$$\gamma_{\alpha s}=\gamma_{\beta s}+\gamma_{\alpha\beta} \cdot$$

The thickness of the β wetting layer then has an infinite or macroscopic value. This transition from partial to complete wetting arises from the preferential affinity of one of the phases for the wall and can be either continuous or first order, depending on material and substrate parameters. Similar transitions can occur in semi-infinite Ising models below T_c,[14] and in condensation out of the gas phase on an attractive substrate.[5,15]

More recently, it has been shown that semi-infinite systems which undergo a first-order bulk transition can exhibit an interesting new type of surface phase transition.[7–10] Although the bulk order parameter is discontinuous at the transition temperature $T=T^*$, it may happen that the surface order parameter behaves continuously. Furthermore, as T^* is approached from below in this case, a layer of the disordered phase intervenes between the free surface and the ordered bulk. At $T=T^*$ the interface between ordered bulk and the disordered surface phase becomes delocalized and diffuse, as at the wetting transition.

In the present paper we investigate the relationship between wetting and SID transitions. In Sec. II the Landau free-energy functionals for the two types of transitions are described and it is shown how one can be mapped into the other by an appropriate transformation of the coupling constants. The relationship between the scaling variables in the two models is derived and the connection between the scaling laws is made explicit. In Sec. III this analysis is extended to include higher-order multicritical phenomena. The relationship between the various multicritical transitions found for certain SID models is clarified and the analysis is extended to higher-order multicritical wetting phenomena. In particular, we show that the inclusion of higher-order symmetry-allowed terms such as $g_1\phi^4$ in the surface contribution to the Landau free-energy functional can lead to new higher-order wetting transitions. Finally, in Sec. IV we utilize the wetting-SID correspondence to obtain new results for the SID transition in two dimensions. The surface exponents are given exactly in this case. One of our most surprising results is that for $d=2$, although the bulk transition is first order, the surface order parameter *always* behaves continuously.

II. WETTING-SID EQUIVALENCE: CRITICAL AND TRICRITICAL PHENOMENA

We consider a d-dimensional semi-infinite system with a $(d-1)$-dimensional free surface. The z axis is taken perpendicular to the free surface. The generic form of the Landau free-energy functional that we consider is[16]

$$F\{\phi\}=\int_0^\infty dz \int d^{d-1}r[\tfrac{1}{2}(\nabla\phi)^2+f(\phi)+\delta(z)f_1(\phi)] \ , \quad (2)$$

where ϕ is a one-component order parameter. $f(\phi)$ is the bare bulk free-energy density for a homogeneous field configuration ϕ, and $f_1(\phi)$ is a surface contribution containing the influence of the wall or surface on the order-parameter field.

In the mean-field (MF) approximation[1,7,17] the order parameter profile $m(z)\equiv\langle\phi\rangle$ is determined from $\delta F/\delta\phi\,|_m=0$. This leads to

$$\frac{dm}{dz}=\pm[2f(m)-2f(m_b)]^{1/2} \ , \quad (3a)$$

where m_b is the bulk value of the order parameter. For $z\to 0+$, the order-parameter profile has to satisfy the boundary condition

$$\left.\frac{dm}{dz}\right|_0=\left.\frac{\partial f_1(m)}{\partial m}\right|_{m_1} \ , \quad (3b)$$

with $m_1\equiv m(z=0)$. Combining (3a) and (3b) one finds that m_1 is determined by

$$\frac{\partial f_1(m_1)}{\partial m_1}=\pm[2f(m_1)-2f(m_b)]^{1/2} \ , \quad (4)$$

for $m_1 \lessgtr m_b$. Order-parameter profiles which satisfy (3a) and (4) and yield the absolute minimum of the free energy describe the thermodynamic state of the system.

We consider first the wetting transition. $f(\phi)$ then has the form

$$f(\phi)=-\frac{\tau}{2}\phi^2+\frac{g}{4}\phi^4-h\phi \ . \quad (5a)$$

We are in the ordered phase so that the reduced temperature τ, measuring the distance from T_c, the bulk ordering temperature, is positive. h is proportional to the chemical-potential difference from coexistence; in the magnetic language used here it is the bulk magnetic field.

The contributions to $f_1(\phi)$ are due to the free surface or wall and are of two types. First, the semi-infinite geometry modifies the interactions between "spins" near the surface. In the continuum model we consider this may be taken into account by an incremental surface-temperature field τ_1 localized on the surface. τ_1 is also called the inverse extrapolation length. The second effect may be described by a local chemical potential or surface field h_1 which describes the affinity of the surface or wall for the surface phase. $f_1(\phi)$ is therefore taken to have the form

$$f_1(\phi)=\tfrac{1}{2}\tau_1\phi^2-h_1\phi \ . \quad (5b)$$

If the bulk boundary conditions far from the surface favor one phase (up spins for example), and if h_1 is negative, then at sufficiently low temperatures a layer of down spins with finite thickness may partially wet the surface. The wetting transition occurs when at some temperature $T<T_c$ the thickness of this wetting layer diverges (for $h=0$). The down-spin phase then completely wets the surface. h and h_1 must therefore be taken to have opposite signs in (5). In the following we take $h\geq 0$ and $h_1\leq 0$. In addition, we consider only surface enhancement, $\tau_1>0$. In this case a MF analysis of (2) and (5) yields either critical or first-order wetting depending on the specific values of τ_1, h_1, and τ.

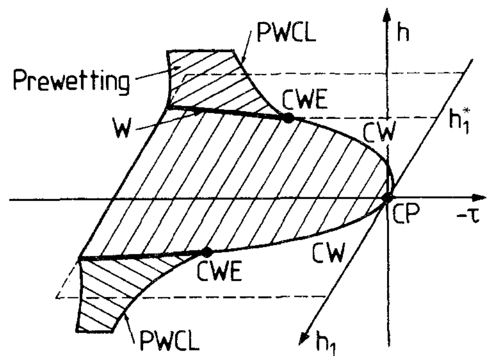

FIG. 1. Surface phase diagram in (τ,h_1,h) space for fixed subcritical surface enhancement $\tau_1>0$ obtained in the MF approximation for $F\{\phi\}$ given by (2), (5a) and (5b). Point CP at the origin is the "ordinary transition" at which the bulk orders. CWE-CP-CWE parabola in the $h=0$ plane is the line of critical interface delocalization transitions. The CW or critical wetting transition occurs if the parabola is crossed for $|h_1|<|h_1^*|$. For $|h_1|=|h_1^*|=\tau_w\sqrt{2/g}$ (or $\tau_1=\sqrt{2\tau_w}$) the transition occurs at the CWE, the critical wetting endpoint (a tricritical point), and for $|h_1|>|h_1^*|$ the transition at coexistence is first order (W). For $|h_1|>|h_1^*|$ there is a prewetting surface at finite h; crossing this surface there is a finite jump in the coverage. Front edge of this surface is called the PWCL, or prewetting critical line.

It should be emphasized that our choice of $F\{\phi\}$ presupposes that all interactions are short ranged. The van der Waals interactions present in real (nonmagnetic) systems are not short ranged in this sense. In particular, for van der Waals interactions the substrate potential h_1 has a long-range component which drops off as z^{-3} for $d=3$. This long-range component does not effect the wetting-SID equivalence, but it does in general modify certain aspects of the critical behavior.[6,18]

The MF theory for the Landau free-energy functional $F\{\phi\}$ given by (5a) and (5b) has been discussed in Refs. 1 and 17. The corresponding phase diagram is shown in Fig. 1. The point CP at the origin of Fig. 1 is the "ordinary transition" at which the bulk orders. The CWE-CP-CWE parabola in the $h=0$ plane is the line of critical interface delocalization transitions. For $|h_1|<|h_1^*|$ and $h=0$ we have the critical wetting (CW) transition at $\tau_w=g(h_1/\tau_1)^2$. For $\tau>\tau_w(h_1)$ there is incomplete wetting at coexistence and for $\tau<\tau_w$ complete wetting. In Fig. 2(a) the order-parameter profile $\phi(z)$ is shown for $\tau\gtrsim\tau_w$ near the CW transition. As the transition is approached from below, the coverage m_s, which is proportional to the distance of the interface from the surface, diverges as

$$m_s\sim\begin{cases}(\tau-\tau_w)^{\beta_s}, & \tau\to\tau_w^+,\ h=0\\ h^{1/\delta_s}, & \tau=\tau_w,\ h\to 0+ \ .\end{cases}$$

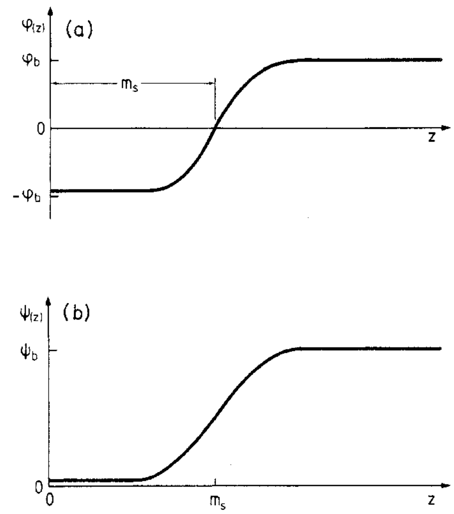

FIG. 2. (a) Order-parameter profile $\phi(z)$ for $\tau \gtrsim \tau_w$ near the CW transition. ϕ_b is the bulk value of the order parameter and m_s, the distance of the interface from the surface, is the coverage. $\phi(z=0)+\phi_b \rightarrow 0$ and $m_s \rightarrow \infty$ at the wetting transition. (b) Order-parameter profile $\psi(z)$ for $a \lesssim a^*$ near the SID transition O_2. ψ_b is the bulk value of the order parameter. $\psi(z=0) \rightarrow 0$ at the SID transition.

Off coexistence ($h \neq 0$) there is no transition. For $|h_1|=|h_1^*|=\tau_w\sqrt{2/g}$ (or $\tau_1=\sqrt{2\tau_w}$) the transition occurs at the critical wetting endpoint (CWE) and for $|h_1|>|h_1^*|$, the transition at coexistence is first order. The CWE is a tricritical point.

For $|h_1|>|h_1^*|$ the phase diagram has a prewetting surface at finite h. The front edge of this wing is called the prewetting critical line (PWCL). Crossing the prewetting wing there is a finite jump in the coverage. These and other aspects of the phase diagram have been discussed in detail elsewhere.[5]

In the vicinity of the CW and CWE transitions the singular part of the surface free-energy density F_s has the scaling form[19,20]

$$F_s = t^{2-\alpha_s}\Sigma(ht^{-\Delta}, vt^{-\Delta_1}) , \quad (6)$$

where t, h, and v are appropriate scaling fields which respect the symmetries and vanish at the transition. At the CW transition there are two relevant scaling fields. One measures the distance from the CW line in the symmetry plane and the other measures the distance perpendicular to the coexistence plane. Two independent exponents, α_s and Δ, are therefore needed to describe the relevant scaling behavior in this case. At the CWE there is an additional relevant field which measures the distance from the CWE along the CW critical curve, and three exponents, α_s, Δ, and Δ_1, are required to describe scaling.

MF theory yields an explicit form for (6). Near the CW transition we have[8,9,21]

$$F_s \sim t^2\Sigma_1(ht^{-2}) - h\ln[t\Sigma_2(ht^{-2})] , \quad (7)$$

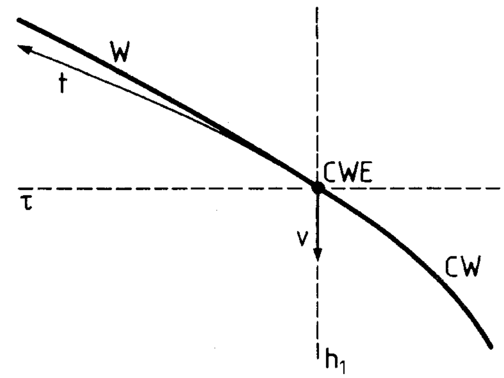

FIG. 3. Detail of the wetting surface phase diagram shown in Fig. 1 in the neighborhood of the CWE. t and v are tricritical scaling fields. t points along the continuation of the parabola CP-CW-CWE and v measures the distance from the phase boundary in the symmetry plane $h=0$.

where $t>0$ is a measure of the distance from the CW line in the symmetry plane $h=0$. For constant τ_1 and g, an appropriate choice of a linear scaling field t would be

$$t = \delta\tau - \frac{2gh_1^w}{\tau_1^2}\delta h_1 ,$$

where $\delta\tau = \tau - \tau_w$, $\delta h_1 = h_1 - h_1^w$, and $\tau_w = g(h_1^w/\tau_1)^2$ is the equation of the delocalization critical line. t points inside the phase-boundary curve so that $\delta\tau > 0$ and $-h_1^w\delta h_1 > 0$. In general, if τ_1 is allowed to vary, $\delta\tau_1$ also has a projection on t. τ_1 and h_1 are thus nonordering fields which have the same scaling dimension as t.[22]

Utilizing (6) and (7) we see that $\alpha_s=0$ and $\Delta=2$ at the CW transition in the MF approximation. A rather unusual feature of this transition is that MF theory yields logarithmic divergences in nonlocal quantities such as F_s or m_s,

$$F_s \sim h\,|\ln h| ,$$

for $t=0$, and

$$m_s \equiv \frac{\partial F_s}{\partial h} \sim \begin{cases} |\ln t| , & h=0 \\ |\ln h| , & t=0 . \end{cases}$$

Since δh_1 is a nonordering field, exponents for the singular part of the surface magnetization $m_1 \equiv \partial F_s/\partial h_1$ are given in terms of α_s.[22] For example, $\beta_1 = 1-\alpha_s = 1$ and $\gamma_{11} = \alpha_s = 0$ in the MF approximation.

At the CWE, MF theory yields the following form for the singular part of the free-energy density[8,9,21]:

$$F_s \sim t^3\Sigma_1(ht^{-3}, vt^{-2}) - h\ln[t\Sigma_2(ht^{-3}, vt^{-2})] . \quad (8)$$

Here, t is a scaling field along the continuation of the parabola CP-CW-CWE and v measures the distance from the phase boundary in the symmetry plane $h=0$ (see Fig. 3).[23,24] In Fig. 3 the v axis is drawn in the h_1 direction; this is an arbitrary choice and in general all that is necessary is that v not be parallel to t at the CWE. When $t \rightarrow 0$

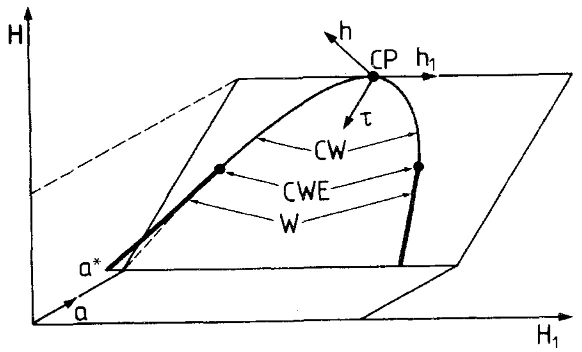

FIG. 4. SID phase diagram obtained from the wetting phase diagram in Fig. 1 using the coupling-constant transformation (11). The SID transition occurs for $H=H_1=0$, i.e., where the a axis cuts the coexistence plane.

with $v=0$ the CWE is approached *tangentially* to the phase boundary, whereas an increase in v results in departure from the CWE *and* the phase boundary. This implies that if $\delta\tau$, δh_1, and $\delta\tau_1$ denote the deviations of these three coupling constants from their values at the CWE, then in general all three have projections on both v and t.

From (6) and (8) we see that $\alpha_s=-1$, $\Delta=3$, and $\Delta_1=2$ in the MF approximation. In addition, as at the CW transition, MF theory yields logarithmic divergences in the nonlocal quantities F_s and m_s. Other surface exponents follow by differentiation and satisfy scaling relations which may be derived in the usual manner.[19]

Consider now the Landau free-energy functional for the SID transition given by (2) with[7–10]

$$f(\psi)=\tfrac{1}{2}a\psi^2-\tfrac{1}{3}b\psi^3+\tfrac{1}{4}c\psi^4-H\psi \tag{9a}$$

and

$$f_1(\psi)=\tfrac{1}{2}a_1\psi^2-H_1\psi \; . \tag{9b}$$

This model describes systems with a scalar order parameter which allow a cubic invariant. In addition, this model also describes a larger class of multicomponent systems in situations where the disordered phase is in coexistence with one of the ordered phases, as discussed in Refs. 8 and 10 for the q-state Pott's model. In this case ψ is the amplitude of the ordered component of the multicomponent order parameter and H and H_1 (both ≥ 0) couple only to this component. If the fields conjugate to the other components of the order parameter are not identically zero the phase diagram is considerably more complicated.[8] This aspect of the problem will not be discussed here.

If we make the substitution

$$\psi=\phi+\frac{b}{3c} \; , \tag{10}$$

we obtain (5) with

$$\tau=-a+\frac{b^2}{3c} \; , \tag{11a}$$

$$g=c \; , \tag{11b}$$

$$h=H+\frac{b}{3c}\left[\frac{2b^2}{9c}-a\right] , \tag{11c}$$

$$\tau_1=a_1 \; , \tag{11d}$$

$$h_1=H_1-\frac{b}{3c}a_1 \; . \tag{11e}$$

With the use of this coupling-constant transformation, the SID phase diagram for the model described by the free-energy functional [(2) and (9)] can be obtained from the phase diagram for the model [(2) and (5)] given in Fig. 1. This SID phase diagram is shown in Fig. 4. The coexistence plane $h=0$, $\tau>0$ in Fig. 1 is now given by

$$H=\frac{b}{3c}(a-a^*) \; ,$$

with $a^*\leq a\leq b^2/(3c)$ and $a^*\equiv 2b^2/(9c)$.

The SID transitions considered in Refs. 7–10 occur at $H=H_1=0$, i.e., where the a axis cuts the coexistence plane in Fig. 4. This happens at $h=0$, or $a=a^*=2b^2/(9c)$. In fact, this intersection is *always* along the parabola CP-CW-CWE or, for $a_1<(a^*)^{1/2}$, its extension—given by the dashed curve in Fig. 4. This can be seen by noting that the CW parabola in Fig. 1 is given by

$$\tau=g(h_1/\tau_1)^2 \; . \tag{12}$$

For $a=a^*$ and $H_1=0$, (11) implies $\tau(a^*)=b^2/(9c)$ and $h_1=-a_1b/(3c)$, so that (12) is fulfilled.

For $\tau_1>[2\tau(a^*)]^{1/2}$, or equivalently, $a_1>(a^*)^{1/2}$, the intersection is along the CW curve. This is the SID transition O_2. For $a_1=(a^*)^{1/2}$ the intersection is at the CWE. The corresponding SID transition is called $\bar{S}$.[7–9] For $a_1<(a^*)^{1/2}$ the intersection is along the dashed curve in Fig. 4. This corresponds to a point of incomplete wetting, and the SID transition—called O_1—is first order in this case.

The singular behavior at $\bar{S}$ and O_2 discussed in Refs. 7–9 can also be obtained from the above analysis. Consider first the O_2 transition (CW). From Fig. 4 it is easy to see that neither a nor H lie in the symmetry plane of the delocalization curve. A general variation of these fields therefore has projections on *both* scaling fields t and h in (6). Since h has the larger scaling dimension, the response to a and H is determined by the scaling variable h. In Ref. 8 this scaling variable has been denoted by

$$u=\delta a-\frac{3c}{b}H=-\frac{3c}{b}h \; ,$$

where $\delta a\equiv a-a^*$. Only for the special combination of δa and H which yields $u=0$ is the response determined by the scaling variable t. H_1, however, is in the symmetry plane and its scaling dimension is therefore the same as that of t. *There exists, therefore, the correspondence* $h\sim|u|$ *and* $t\sim H_1$ *between the scaling variables at these two transitions.*

The singular part of the surface free-energy density at the CW transition is given by

$$F_s=t^{2-\alpha_s}\Sigma(ht^{-\Delta})=h^{(2-\alpha_s)/\Delta}\Omega(th^{-1/\Delta}) \; . \tag{13}$$

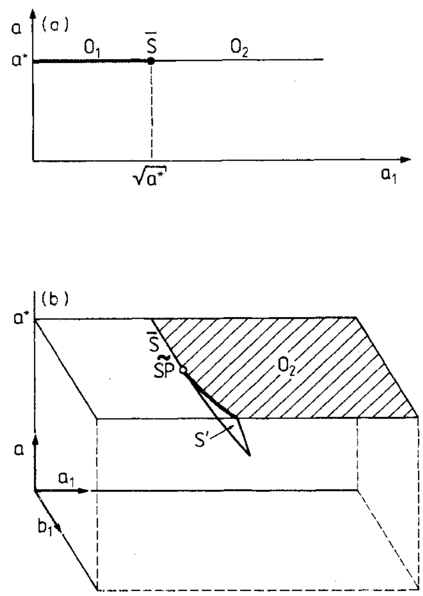

FIG. 5. SID phase diagrams in (a,a_1,b_1) space obtained in the MF approximation for $F\{\psi\}$ given by (2) and (15) with $(x,y)=(3,4)$. The bulk is ordered for $a<a^*$. (a) For $b_1=c_1=0$ there is a critical line (O_2) which ends at a tricritical point $\bar{S}$ with coordinates $[a^*,(a^*)^{1/2}]$. For $a_1<(a^*)^{1/2}$ the surface transition is first order. (b) $b_1,c_1>0$. The O_2 transition occurs if the $a=a^*$ plane is crossed in the shaded region. There is a tricritical *line* $\bar{S}$ which ends at a fourth-order multicritical point $\widetilde{SP}$ with coordinates $[a^*,(a^*)^{1/2},\sqrt{c/2}]$. The surface transition is first order if the $a=a^*$ plane is crossed in the unshaded region.

For the corresponding SID transition O_2, the singular part of F_s is given by[8]

$$F_s=|u|^{2-\bar{\alpha}_s}\bar{\Omega}(H_1|u|^{-\bar{\Delta}_1}), \tag{14}$$

where we have used overbars to indicate exponents at the SID transition. From (13) and (14) we see that $2-\bar{\alpha}_s=(2-\alpha_s)/\Delta$ and $\bar{\Delta}_1=1/\Delta$. Furthermore, since $|u|$ measures *both* temperatures *and* field deviations at the O_2 transition, we find, for example,

$$\bar{\beta}_1=2-\bar{\alpha}_s-\bar{\Delta}_1=(1-\alpha_s)/\Delta$$

and

$$\bar{\beta}_s=1-\bar{\alpha}_s=(2-\alpha_s-\Delta)/\Delta .$$

Other relations between the various exponents are easily derived in a similar manner.

A similar analysis can be applied to the tricritical transition $\bar{S}$(CWE). General variations in a and H have projections on all three variables t, v, and h in (6). Since h again has the largest scaling dimension, the response to a general variation in a or H will be determined by the scaling variable h. Similar arguments show that the response to H_1 is given by the scaling variable v. The singular part of F_s at $\bar{S}$ is given by[8]

$$F_s=|u|^{2-\bar{\alpha}_s}\bar{\Omega}(H_1|u|^{-\bar{\Delta}_1},\delta a_1|u|^{-\bar{\phi}_a}),$$

where δa_1 is the scaling field at the tricritical point $\bar{S}$ parallel to the critical line O_2. *At* $\bar{S}$, *we therefore have the correspondence* $h\sim|u|$, $v\sim H_1$, *and* $t\sim\delta a_1$. Rewriting (6) in the form

$$F_s=h^{(2-\alpha_s)/\Delta}\Omega(th^{-1/\Delta},vh^{-\Delta_1/\Delta}),$$

we see that $2-\bar{\alpha}_s=(2-\alpha_s)/\Delta$, $\bar{\Delta}_1=\Delta_1/\Delta$, and $\bar{\phi}_a=1/\Delta$, where all exponents are tricritical exponents.

Previous work on wetting has been primarily concerned with nonlocal or excess surface quantities such as the coverage m_s. On the other hand, the most interesting aspect of the SID transitions is the critical behavior of *local* surface quantities.[7–9] For instance, the local order parameter at the surface $M_1\equiv\partial F_s/\partial H_1=\langle\psi(r,z=0)\rangle$ goes continuously to zero with the exponent $\bar{\beta}_1=2-\bar{\alpha}_s-\bar{\Delta}_1$ [see Fig. 2(b)],

$$M_1\sim|u|^{\bar{\beta}_1}.$$

From (10) and (11), it follows that the corresponding quantity for wetting is

$$\eta\equiv m_1+\frac{b}{3c}=m_1+m_b(\tau_w),$$

with $m_1\equiv\langle\phi(r,z=0)\rangle$ and $m_b(\tau_w)=\sqrt{\tau_w/g}$. $\eta\sim\partial F_s/\partial h_1$ is just what we mean by the singular part of the surface order parameter in the wetting problem [see Fig. 2(a)]. This quantity vanishes as

$$\eta\sim\begin{cases}(\tau-\tau_w)^{\beta_1}, & \tau\to\tau_w^+,\ h=0\\ h^{1/\delta_1}, & \tau=\tau_w,\ h\to0+ .\end{cases}$$

At the CW transition $\beta_1=1-\alpha_s$ and $1/\delta_1=(1-\alpha_s)/\Delta$ and at the CWE, $\beta_1=(2-\alpha_s-\Delta_1)/\Delta_1$ and $1/\delta_1=(2-\alpha_s-\Delta_1)/\Delta$ (where in the last two expressions all exponents are tricritical exponents).[25] Since the SID scaling field $|u|$ corresponds to h at both these transitions we have $\bar{\beta}_1=1/\delta_1$.

Finally, it should be emphasized that the wetting-SID equivalence discussed in this section is *not* restricted to the MF approximation. In both cases, the important fluctuations which invalidate the MF approximation arise from capillary waves—long-wavelength interface fluctuations. Because of this fact effective interface models for these two transitions, with the appropriate transformation of coupling constants discussed above, are, in fact, the same.[26,27]

III. HIGHER-ORDER MULTICRITICAL PHENOMENA

In the context of SID transitions, a larger class of models than that described by (9) have been considered. The general parametrization discussed in Refs. 7–10 is

$$f(\psi)=-H\psi+\tfrac{1}{2}a\psi^2-\frac{1}{x}b\psi^x+\frac{1}{y}c\psi^y \tag{15a}$$

and

$$f_1(\psi)=-H_1\psi+\tfrac{1}{2}a_1\psi^2-\frac{1}{x}b_1\psi^x+\frac{1}{y}c_1\psi^y , \tag{15b}$$

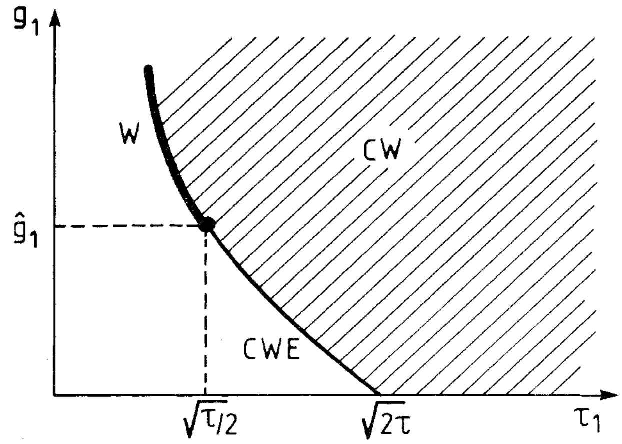

FIG. 6. MF wetting phase diagram in (τ, g_1) space for $f_1(\phi)=-h_1\phi+\frac{1}{2}\tau_1\phi^2+\frac{1}{4}g_1\phi^4$. There is now a CWE *line* which ends in a fourth-order multicritical point with coordinates $(\tau_1,g_1)=(\sqrt{\tau/2},g/(3\sqrt{2\tau}))$. CW occurs if the critical hypersurface is crossed in the shaded region.

with b, c, a_1, b_1, and c_1 all positive and ψ a scalar order-parameter field.

The case $(x,y)=(3,4)$ with $b_1=c_1=0$ was discussed above. The general wisdom is that the inclusion of terms of higher order than ψ^2 in f_1 does not change the critical behavior in semi-infinite systems: They are irrelevant operators. Here, however, this is *not* the case. For finite b_1, $c_1>0$ additional higher-order multicritical phenomena have been found.[7-10] The corresponding phase diagram is shown in Fig. 5. For $b_1=c_1=0$ we have a critical line (O_2) which ends at the tricritical point $\bar{S}$. For smaller values of a_1 the transition is first order [Fig. 5(a)]. For finite b_1,c_1 the phase diagram is shown in Fig. 5(b).[8] The O_2 transition occurs if the $a=a^*$ plane is crossed in the shaded region. The point $\bar{S}$ becomes a tricritical *line* which ends at a fourth order multicritical point $\widetilde{SP}$ with coordinates $(a^*,(a^*)^{1/2},\sqrt{c/2})$. For larger values of b_1 there is a wing S' which extends into the low-temperature phase. The MF exponents for the $\widetilde{SP}$ point are given in Refs. 7 and 8.

In exactly the same way, a term $g_1\phi^4/4$ in the surface contribution $f_1(\phi)$ to the Landau free energy is relevant at the wetting transitions. For $f(\phi)$ given by (5a) and

$$f_1(\phi)=-h_1\phi+\tfrac{1}{2}\tau_1\phi^2+\tfrac{1}{4}g_1\phi^4\ ,$$

the MF equation [Eq. (4)] for the surface order parameter $\eta=m_1+m_b$ is easily derived. As a result, one obtains the phase diagram shown in Fig. 6. Instead of a single point, there is now a line of CWE transitions given by

$$g_1(\tau_1)=\frac{g}{3\tau}(\sqrt{2\tau}-\tau_1)\ ,$$

where $\sqrt{\tau/2}<\tau_1<\sqrt{2\tau}$. This line ends at a fourth-order multicritical point with coordinates $(\tau_1,g_1)=(\sqrt{\tau/2},g/(3\sqrt{2\tau}))$. The critical hypersurface in which these transitions occur is given by

$$g_1m_b^3+\tau_1m_b+h_1=0\ ,$$

with

$$m_b=\sqrt{\tau/g}\ .$$

This new fourth-order multicritical point corresponds to the $\widetilde{SP}$ point discussed for SID above. At this point there are four relevant perturbations and the singular part of the surface free-energy density has the scaling form

$$F_s\sim t^{2-\alpha_s}\Sigma(ht^{-\Delta},vt^{-\Delta_1},wt^{-\phi_1})\ .$$

Let t be the scaling variable asymptotically parallel to the tricritical line leading to the multicritical point and take h, v, and w to be the limiting orientation of the scaling directions for the tricritical line as the fourth-order critical point is approached.[23] MF theory then gives the values $\alpha_s=-2$, $\Delta=4$, $\Delta_1=3$, and $\phi_1=2$ for the critical exponents. In addition, F_s and m_s again have logarithmic divergences as at the other wetting transitions.

With the scaling field transformation $t\sim\delta b_1$, $h\sim|u|$, $v\sim|h_1|$, and $w\sim\delta a_1$, these results are the same as those found in Refs. 7 and 8 for the $\widetilde{SP}$ transition with $(x,y)=(3,4)$. At this transition the corresponding exponents are related by $2-\bar{\alpha}_s=(2-\alpha_s)/\Delta$, $\bar{\Delta}_1=\Delta_1/\Delta$, $\bar{\phi}_a=\phi_1/\Delta$, and $\bar{\phi}_b=1/\Delta$.

The other model discussed in Refs. 7–9, given by (15) with $(x,y)=(4,6)$, describes systems with a bulk tricritical point. Here again, various multicritical SID behavior was found to be possible for special values of the surface coupling constants. In fact, the exponents for the $\bar{S}$ and $\widetilde{SP}$ transitions in this case are *different* from those for these transitions with $(x,y)=(3,4)$. The reason is that here, $\bar{S}$ and $\widetilde{SP}$ correspond to *still higher-order critical points.* This is due to the absence of a ψ^3 term in the Landau free-energy functionals. Consider the MF scaling form of the surface free-energy density at the fourth-order multicritical point discussed above,

$$F_s\sim t^4\Sigma(ht^{-4},vt^{-3},wt^{-2})\ . \qquad (16)$$

For the SID transition the scaling variable t is along the δb_1 direction, i.e., the scaling field is proportional to the cubic-term coupling constant in $f_1(\psi)$. This field is absent (i.e., zero) for $(x,y)=(4,6)$. For $t=0$, (16) becomes

$$F_s\sim h\tilde{\Omega}(vh^{-3/4},wh^{-1/2})\ .$$

With the scaling-field correspondence $h\sim|u|$, $v\sim h_1$, and $w\sim\delta a_1$, this is precisely the form found in Ref. 8 for the $\bar{S}$ transition in the (4,6) model. The $\bar{S}$ transition for $(x,y)=(4,6)$ can therefore be interpreted as a fourth-order critical line with one of its scaling variables missing (set equal to zero). Because of the particular parametrization of the model, the phase diagram is a slice of the phase diagram for a model exhibiting the full sequence of multicritical points. A similar analysis may be applied to the $\widetilde{SP}$ transition in the (4,6) model and is clearly generalizable to other special cases.

All SID transitions are thus special cases of general interface delocalization transitions in semi-infinite systems.

The embedding of the SID transition in the higher-dimensional phase space (as in Fig. 4) describing these delocalization transitions is quite useful for identifying the scaling directions and helping us better understand the resulting phenomena. In the next section we utilize this equivalence to determine the critical exponents for the SID transition O_2 in two dimensions.

IV. SID TRANSITIONS IN $d=2$

There already exists considerable literature concerning interface wetting or pinning transitions in two dimensions.[14,18,28] The key feature in two dimensions is the absence of all phase transitions at $T>0$ away from coexistence. Away from bulk coexistence, surface behavior is $d-1=1$ dimensional and thus cannot support phase transitions at finite temperatures.[5] This implies that in the phase diagram in Fig. 1, the CWE and wetting lines are absent. Only the CW transition remains. Further, this implies, with the use of the wetting-SID equivalence, that *all* SID transitions are *continuous* in $d=2$. In Fig. 5(a), the $O_1,\bar{S}$ parts of the phase diagram in the a,a_1 plane are absent and the O_2 line extends down to zero a_1. This is a rather surprising feature of the SID transition in two dimensions.

Our detailed understanding of the CW transition in $d=2$ comes from the analysis of nearest-neighbor Ising lattice-gas models[14] and a still simpler, closely related class of models based on the solid-on-solid (SOS) approximation.[28] These SOS models can be easily solved in $d=2$ for a wide range of substrate potentials as well as finite bulk field h. The wetting transition corresponds to the thermal unbinding of the interface from a potential well which characterizes the effect of the negative surface field h_1 in (5b). For short-range substrate potentials—equivalent to pure surface fields as in (5b)—the analysis of these models shows that the singular part of the surface free-energy density has the scaling form[18]

$$F_s \sim t^2\Sigma(ht^{-3}) ,$$

so that $\alpha_s=0$ and $\Delta=3$. For SID transitions, this implies $\bar{\alpha}_s=\frac{4}{3}$ and $\bar{\Delta}_1=\frac{1}{3}$, and furthermore, $\bar{\beta}_1=\frac{1}{3}$ and $\bar{\beta}_s=-\frac{1}{3}$. Other exponents may be obtained using the correspondence discussed in Sec. II.

V. CONCLUSIONS

Wetting and SID transitions are two intimately related types of interface delocalization phenomena in semi-infinite systems. In particular, as shown in the text, there exists a direct relationship between the scaling variables and scaling laws at these transitions. Furthermore, this wetting-SID equivalence is not based solely on the MF approximation; it can be shown that effective interface models for wetting and SID transitions are, in fact, the same. With the transformation of scaling variables derived in Secs. II and III it is straightforward to translate results for one phenomena to the other.

This equivalence should be particularly useful when seeking semi-infinite systems which exhibit interface delocalization transitions. While wetting transitions have been observed in binary mixtures[29] and in multilayer adsorption phenomena on attractive substrates,[30] the best candidates for a detailed experimental study of critical wetting may well be systems exhibiting SID transitions. Quantitative measurements of local surface quantities such as the value of the order parameter on the surface are, in general, easier to perform than measurements of nonlocal or excess quantities such as the surface free-energy density or the coverage. Systems with SID transitions are particularly well suited for such measurements since the surface order parameter M_1 goes to zero at the transition. Methods such as low-energy electron diffraction[31] (LEED) and spin-polarized LEED,[32] which have already been successfully applied to study critical phenomena in semi-infinite systems, should be directly applicable in this case. Particularly good candidates could be binary-alloy crystals with a discontinuous bulk order-disorder transition. In fact, LEED measurements on the {100} surface of a Cu_3Au crystal do seem to indicate a continuous SID transition at the bulk first-order order-disorder transition.[33,34] Present measurements are too imprecise to yield detailed information on the behavior of the surface order parameter, but recent improvements in LEED and spin-polarized LEED should make it possible to obtain accurate information concerning the exponent $\bar{\beta}_1$. This would be extremely useful since our understanding of these transitions in three bulk dimensions is still far from complete.[26,27,35,36]

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