Multicriticality of Wetting, Prewetting, and Surface Transitions

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The global phase diagram for wall and surface critical phenomena is analyzed in the space of temperature, surface enhancement, and bulk and surface fields, on the basis of Landau phenomenological theory. Features probably valid for various real systems are the physical unity of prewetting and pure surface criticality, and novel exponents for critical wetting and for a *wetting tricritical point*, which terminates the region of normal first-order wetting.

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Critical behavior near the walls and surfaces of a macroscopic system is of considerable current interest both theoretically[1] and experimentally.[2,3] In particular, if, say in a ferromagnet, the coupling between spins near the surface is sufficiently enhanced relative to the bulk coupling, a purely "surface transition" will occur in which the spins near the wall undergo a *continuous* or critical ordering transition (*above* the bulk transition at T_c^{∞}) while the bulk remains disordered.[4] The corresponding phase diagram is shown in Fig. 1(a) where $t \propto T - T_c^{\infty}$ measures the temperature and $g \propto J_1 - J_{1,c}$ represents the enhancement of the surface coupling, J_1, over the "special" value, $J_{1,c}$, at which the surface transition splits off. For $g<0$, surface and bulk order together at an "ordinary" transition.[4b] Surface transitions are believed to underlie phenomena such as surface reconstruction, and surface segregation in binary alloys,[5] and may also occur in polymer solutions and percolating systems.[6]

Surface "wetting" transitions, on the other hand, were recently predicted[7] and have now been seen in experiments on fluid systems.[8] A wetting transition occurs when, under variation of temperature (or composition, etc.), the angle of contact, $\alpha\hat{\beta}\gamma$, made by the interface between two coexisting phases, α and β, and a wall or bounding phase, γ, becomes identically zero. Correspondingly, the interfacial tensions, which usually satisfy $\sigma_{\alpha\gamma} < \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ (partial wetting), attain the complete wetting limit, $\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$. Wetting transitions are normally of *first order*,[7] in that the thickness, l_W, of the β-like wetting layer increases discontinuously from a finite, microscopic value to an infinite or macroscopic value. Wetting stems from the preferential affinity of one chemical species for the wall; if $\sigma_{\alpha\beta}(T) \to 0$, as in a critical region, the preference has an overwhelming effect.

The simplest models for wetting[7,9] introduce an incremental chemical potential, $\delta\Delta\mu = h_1 k_B T$, which favors one species and acts only near the wall. Within approximations of van der Waals, mean field, or Landau character, phase diagrams like Fig. 1(b) are usually generated: here $h = (\Delta\mu - \Delta\mu_\sigma)/k_B T$ measures the deviation of the bulk chemical potential difference from coexistence. (In a ferromagnet $H = hk_B T$ and $H_1 = h_1 k_B T$ represent bulk and surface magnetic fields.) Evidently the wetting transition, W, is connected by a line of first-order "prewetting" transitions

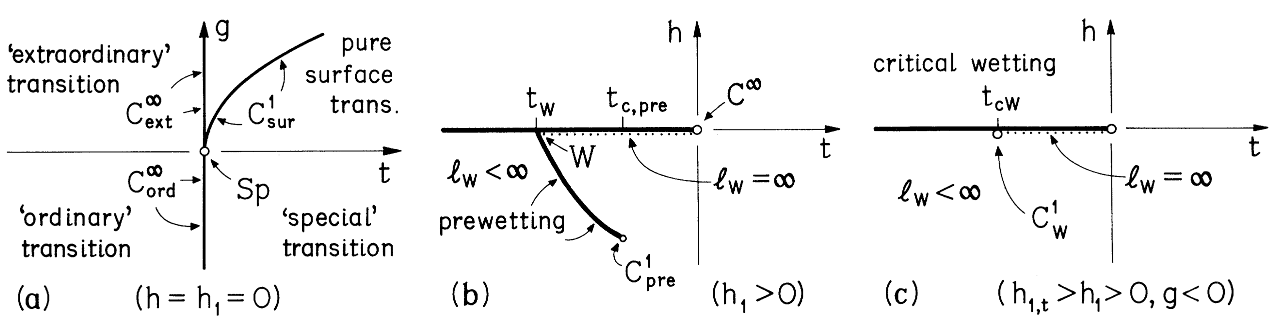

FIG. 1. Surface phase diagrams in terms of $t \propto T - T_c^{\infty}$, surface enhancement, g, bulk field, h, and surface field, h_1.

(where the jump in l_W is finite) to a "prewetting critical point" (labeled $C_{\rm pre}{}^1$) that is quite distinct from the bulk critical point (labeled C^∞). For certain models,[9,10] however, no prewetting is found and, as illustrated in Fig. 1(c), only a "critical wetting" transition remains at which l_W diverges continuously (when $t \to t_{cW}-$ at $h=0-$). More generally, l_W diverges (logarithmically for short-range potentials) whenever the bulk phase boundary is approached (i.e., $h \to 0-$) above the wetting or critical wetting transitions.

The aim of this note is to elucidate the connections between the seemingly distinct phase diagrams in Fig. 1 which all, nonetheless, result from the presence of a surface that breaks translational symmetry. In particular, we show that prewetting criticality and the pure surface enhanced transitions are essentially the same phenomena. We also describe a "wetting tricritical point"[9] which has unorthodox exponents as does the critical wetting transition. Technically our analysis amounts to an unfolding, within Landau theory, of the "special" surface multicritical point of Lubensky and Rubin[4] into the four-dimensional thermodynamic space (t, h, h_1, g). The resulting global phase diagram is summarized in Fig. 2, where the superscript labels ∞ and 1 distinguish transitions in which, respectively, both bulk and surface or only surface criticality occurs. The surface free-energy density, F_1, in the vicinity of each type of critical or multicritical point scales as

$$F_1(t, h, h_1, g) \approx \tilde{t}^{\,2-\alpha_1}\left(\frac{\tilde{h}}{\tilde{t}^{\Delta}}, \frac{\tilde{h}_1}{\tilde{t}^{\Delta_1}}, \frac{\tilde{g}}{\tilde{t}^{\phi_1}}\right), \qquad (1)$$

where $\tilde{t}$, $\tilde{h}$, $\tilde{h}_1$, and $\tilde{g}$ are appropriate, linear scaling fields[11] which respect the symmetries and vanish at the transition. The basic exponents are listed in Table I; other surface exponents follow by differentiation and satisfy scaling relations such as $\beta_1 = 2 - \alpha_1 - \Delta_1$, $\gamma_1 = \alpha_1 + \Delta + \Delta_1 - 2$, $\eta_\parallel = d - 2\Delta_1/\nu$, etc.[1,12]

Although our analysis rests primarily on Landau theory for a semi-infinite system, which in general can yield correct exponents only for bulk dimensionality $d > 5$, the topology of the global phase diagram is probably essentially correct even for $d = 3$. Furthermore, the intrinsic character of the various transitions, together with renormalization-group $\epsilon = 4 - d$ calculations,[1] yields plausible exponent predictions for real systems. We present the main results before outlining the analysis.

Consider, first, *supercritical surface enhancement*, $g > 0$ ($J_1 > J_{1,c}$): the phase diagram is shown in Fig. 2(c). A section at fixed $h_1 > 0$ corresponds precisely to the wetting diagram of Fig. 1(b) except that the prewetting critical point will, for small enough h_1, occur *above* bulk criticality ($t_{c,\rm pre} > 0$). Conversely, the t axis corresponds to a fixed, $g > 0$ section of Fig. 1(a). Evidently, then, the *pure surface transition*, $C_{\rm sur}{}^1$, *lies on the prewetting critical line* where this meets the symmetry axis ($h = h_1 = 0$) above $T_c{}^\infty$. For a scalar, ($n = 1$)-component order parameter we thus expect both transitions to display standard ($d-1$)-dimensional Ising-like criticality [so that $\alpha = 0$ (log) and $\Delta = 1\frac{7}{8}$ for $d = 3$]. Likewise $C_{\rm sur}{}^1$ should *not* be a singular point on the line. For a bulk symmetry characterized by $n \geq 2$, however, $C_{\rm sur}{}^1$ should be a *bicritical* point.[11]

For $h_1 \neq 0$ and for *all g*, bulk criticality forces singularities in F_1 on the lines $t = h = 0$, labeled C^∞ in Fig. 2; however, the surface plays only a passive or "driven" role. In particular, only the two bulk fields, t and h, are relevant and the

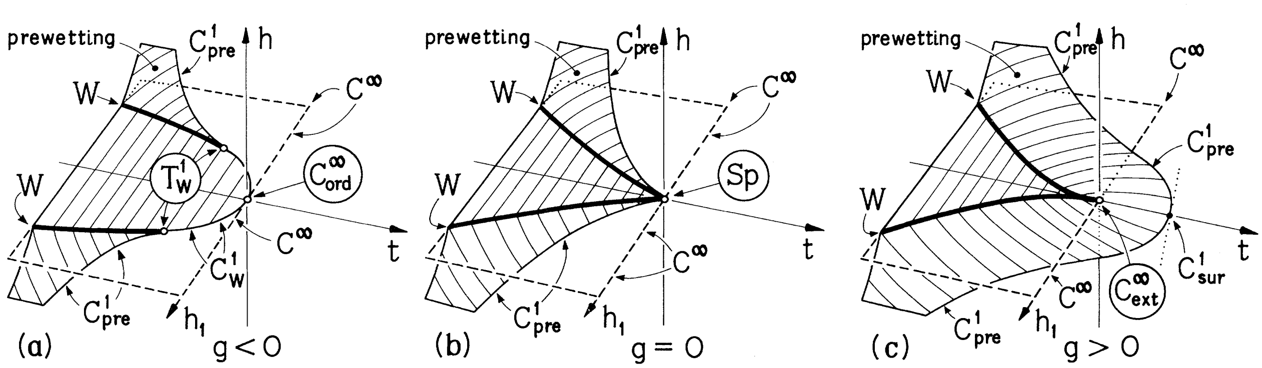

FIG. 2. Sections of the global surface phase diagram for various surface enhancements, g, showing wetting lines, W; critical lines and points, $C_W{}^1$, $C_{\rm pre}{}^1$, $C_{\rm sur}{}^1$, C^∞; and multicritical points (encircled labels).

TABLE I. Surface critical and multicritical points and their exponents. The leading entries and the first terms in the $\epsilon = 4-d$ ($\geqslant 0$) expansions with $n_8 = n+8$ (shown only for Δ_1 and ϕ_1) give the classical, Landau theory values; second entries, involving the bulk d-dimensional exponents $\alpha(d)$, etc., represent the anticipated exact results.

	Critical				Tricritical[a]		Multicritical		
Exponents	Bulk driven C^∞	Surface $C_{\rm sur}^1$	Prewetting $C_{\rm pre}^1$	Wetting C_W^1	Wetting T_W^1	[Pure bulk] T^∞	Ordinary $C_{\rm ord}^\infty$	Special Sp	Extraordinary $C_{\rm ext}^\infty$
α_1	$\frac{1}{2}$, $\alpha(d)+\nu(d)$	0, $\alpha(d-1)$	0, $\alpha(d-1)$	0	$-1^{\rm a}$ $(\frac{1}{2})$	$-1^{\rm a}$ $(\frac{1}{2})$	$\frac{1}{2}$, $\alpha(d)+\nu(d)$	$\frac{1}{2}$, $\alpha(d)+\nu(d)$	$\frac{1}{2}$, $\alpha(d)+\nu(d)$
Δ	$\frac{3}{2}$, $\Delta(d)$	$\frac{3}{2}$, $\Delta(d-1)$	$\frac{3}{2}$, $\Delta(d-1)$	2	3 $(\frac{3}{2})$	$\frac{5}{2}$ $(\frac{5}{4})$	$(\frac{3}{2})$, $\Delta(d)$	$\frac{3}{2}$, $\Delta(d)$	$\frac{3}{2}$, $\Delta(d)$
Δ_1	$\cdots$	$\cdots$	$\cdots$	$\cdots$	2 $(\frac{1}{2})$	2 $(\frac{1}{2})$	$\frac{1}{2}-\frac{4-n}{2n_8}\epsilon+\ldots$	$1+\frac{n-1}{2n_8}\epsilon+\ldots$	$\frac{3}{2}+O(\epsilon)$
ϕ_1	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\frac{3}{2}$ $(\frac{3}{4})$	$\cdots$	$\frac{1}{2}-\frac{n+2}{4n_8}\epsilon+\ldots$	$\cdots$

[a] For $\tilde{h}_1 = 0$ axis parallel to wetting/triple line, $\tilde{t} = 0$ transverse; vice versa in parentheses.

surface order, m_1, does not exhibit a discontinuity when h changes sign below T_c^∞. (This continuity of m_1 for $T_c^\infty > T > T_W, T_{cW}$ becomes less surprising when it is recalled that the wall is already covered with a macroscopically thick layer of $h>0$ phase when h attains $0-$.) When g is positive the prewetting surface and bulk first-order surface intersect at the "extraordinary" multicritical point,[4b] $C_{\rm ext}^\infty$, where three fields are relevant, and meet along the wetting line, which obeys $t_W \sim h_1^{1/\Delta_1}$.

For *marginal* or *critical surface enhancement*, $g=0$, extraordinary and surface transitions merge into the special point where all four fields are relevant. The special point *also* constitutes the common terminus of the wetting and critical prewetting lines [see Fig. 2(b)], which, in terms of the special exponents vary as $t_W \sim t_{c,\rm pre} \sim h_1^{1/\Delta_1}$, $h_{c,\rm pre} \sim h_1^{\Delta/\Delta_1}$.

For *subcritical surface enhancement*, $g<0$, the special point is replaced, at $t=h=h_1=0$, by the much-studied[1,4,12] "ordinary transition," $C_{\rm ord}^\infty$: this nomenclature[4b] is actually somewhat misleading since $C_{\rm ord}^\infty$ has three relevant fields and is thus more singular than the bulk-driven transition, C^∞. As seen in Fig. 2(a), the wetting line now terminates at a new surface multicritical point,[9] T_W^1, at $t_{tW}<0$ and $h_{1,tW} \neq 0$: we term this a *wetting tricritical point*, since, as in superfluid and magnetic tricriticality,[11] a first-order line, namely, wetting in the (t, h_1) plane, turns abruptly at T_W^1 into a critical line, namely, a *line* of *critical wetting*, C_W^1. Notice that a section of Fig. 2(a) at fixed $h_1 < h_{1,tW}$ has precisely the form of Fig. 1(c) (with $t_{cW} > t_{tW}$); for $h_1 > h_{1,tW}$, Fig. 1(b) is again reproduced. Furthermore, note that t_{tW} and $h_{1,tW}$ scale about the special point as $|g|^{1/\phi_1}$ and $|g|^{\Delta_1/\phi_1}$, respectively. Thus models with small h_1 and large negative g can, asymptotically, display *only* critical wetting.

In the tricritical region the prewetting surface represents a "wing"[11] whose critical edge, $C_{\rm pre}^1$, merges into the wetting line as $h_{c,\rm pre} \sim \Delta t^\Delta$ and $\Delta h_1 \sim \Delta t^{\Delta_1}$, when $\Delta t \sim (T_{cW} - T) \to 0+$, where the exponents pertain to T_W^1. Despite the characteristic topology, however, these tricritical wetting exponents are *anomalous* in that they differ from those for bulk tricriticality even within Landau theory (which should be valid for large d): see Table I where both exponent sets are listed. One may presume that wetting tricriticality will also exhibit distinct exponents for $d=3$. Similarly anomalous exponents are found on the critical wetting line (see Table I), which thus should *not* display standard Ising character for any d: a testable prediction.

The Landau theory analysis proceeds by minimizing the phenomenological free-energy functional[1,4b]

$$\mathfrak{F}[m(z)] = D^{-1}\{ \int_0^L dz [\tfrac{1}{2}(dm/dz)^2 + \tfrac{1}{2} t_0 m^2 + u_0 m^4 - hm] - h_1 m_1 - \tfrac{1}{2} g m_1^2 \} \quad (2)$$

with respect to the order-parameter profile, $m(z)$, and boundary value $m_1 \equiv m(0)$, subject to $m(z)$ approaching $m_\infty(t,h)$, an appropriate, stable, uniform bulk solution when $D, z\to\infty$. As usual, one finds $t_0\equiv t$. The enhancement field, g, corresponds here to $-1/\lambda$, where λ is the so-called "extrapolation length"[4b] which sets the boundary condition on $m(z)$; the limit $-1/g\sim\lambda\to 0+$ implies $m(0)=0$. A surface free-energy functional is obtained by subtracting the bulk contribution: it may be written

$$\mathfrak{F}_1[m]=\int_{m_1}^{m_\infty}\left(\frac{dm}{dz}+gm+h_1\right)dm - h_1 m_\infty - \tfrac{1}{2}g m_\infty^2, \quad (3)$$

and evaluated explicitly in terms of m_∞, m_1, and the surd $Q=[2u_0(m_1+m_\infty)^2+h/m_\infty]^{1/2}$; minimization yields

$$gm_1+h_1=-(dm/dz)_1 = \pm(m_1-m_\infty)Q(h,m_\infty,m_1). \quad (4)$$

A graphical analysis[7,9] of these two equations in the phase plane $(m,\dot m\equiv dm/dz)$ reveals most qualitative features of the phase behavior. However, since $\mathfrak{F}_1$ involves $Q(h,m_\infty,m_1)$ explicitly it is not always analytic in m_1 which, otherwise, might be regarded simply as an auxiliary Landau order parameter in an equivalent uniform system. The nonanalyticity leads directly to the novel critical and tricritical wetting exponents. Similarly the singularity in m_∞ at $t=h=0$ (present for all h_1 and g) also yields unorthodox results for C^∞.

In summary, we have exposed the relation between wetting transitions and previously discussed surface critical phenomena. Since the surface field, h_1, and enhancement, g, probably represent various real systems moderately well, our study should be of practical interest. However, even within a mean-field context we have neglected such possibly significant features as a long-range surface attraction[13] and microscopic discreteness.[9,13]

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