PHYSICAL REVIEW B VOLUME 31, NUMBER 7 1 APRIL 1985

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Wetting by critical layers

R. Lipowsky* and U. Seifert
Sektion Physik der Universität München, Theresienstrasse 37, D-8000 München 2, West Germany
(Received 6 August 1984)

Interface depinning transitions such as wetting are described where the surface layer becomes critical as the interface unbinds from the wall. As a consequence, there are two different types of fluctuations, namely, capillary waves and critical fluctuations within the surface layer, which are shown to be governed by two different length scales.

Interface depinning transitions such as wetting have attracted much recent interest.[1–3, 6–14] Such transitions arise at the coexistence curve of several bulk phases if a surface or wall prefers one of these phases and tries to repel the others. At wetting,[2] the substrate surface attracts the adatoms and thus prefers the high-density phase (liquid) to the low-density one (gas). At surface-induced disorder,[3] the surface prefers the disordered phase even in the presence of an ordered bulk, since its effective dimensionality, and thus its tendency to order, is reduced compared to the bulk.

Due to the choosy surface, an interface appears in the semi-infinite system which separates the surface layer from the bulk phase. Under suitable conditions, this interface unbinds from the wall in a continuous manner. As a consequence, various critical effects occur:[3] (1) the thickness $\hat{l}$ of the surface layer diverges; (2) local surface quantities such as the surface-order parameter behave continuously or diverge; (3) long-range correlations build up parallel to the interface, and the interfacial width diverges for $d \leq 3$. The effects (1) and (2) are unique to depinning whereas effect (3) also occurs for a liquid-vapor interface in a weak gravitational field.[4] The critical behavior just described can be characterized by critical exponents. Various theoretical methods have been used in order to calculate these exponents both for systems with short-range[5] and with long-range forces.[6–10] Recently, one such exponent has also been determined experimentally.[11]

Most of the theoretical and experimental work on interface depinning has been concerned with the coexistence of two bulk phases. In addition, some work has been done on depinning near triple points.[11–14] In all cases studied so far, the bulk phases have a finite bulk correlation length. As a consequence, the only important fluctuations are configurational ones of the interface, i.e., capillary waves. In contrast, we will consider here depinning transitions at the coexistence of a critical and noncritical bulk phase. In this case, *two different types of fluctuations* are present, namely, capillary waves and, in addition, critical fluctuations within the surface layer.

Possible candidates for the bulk coexistence of a critical and a noncritical phase are critical end points in binary liquid mixtures.[15,16] At such points, the binary mixture is critical and coexists with the noncritical vapor phase. In the bulk, such a transition may be studied by a Landau-Ginzburg (LG) potential $f(n)$ for the fluid density n with two degenerate minima; the minimum at $n = n_v$ corresponds to the vapor, the one at $n = n_c$ to the critical mixture. For convenience, we will use the rescaled field $\phi \equiv (n - n_c)/(n_v - n_c)$. Thus, the vapor and the critical mixture are given by $\phi = 1$ and $\phi = 0$, respectively.

For a semi-infinite system, the LG free-energy functional has the generic form[1,3]

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

where z denotes the coordinate perpendicular to the surface at $z = 0$. In the present context, the bulk potential f is taken to be

$$f(\phi) = \begin{cases} \tfrac{1}{2}u^2\phi^{2q}, & \phi < \hat{M} , \\ \tfrac{1}{2}\xi^{-2}(1-\phi)^2, & \phi > \hat{M} , \end{cases} \tag{2}$$

where $0 < \hat{M} < 1$ solves $\xi u \hat{M}^q + \hat{M} - 1 = 0$, which guarantees continuity of $f(\phi)$ at $\phi = \hat{M}$. ξ is the finite bulk correlation length within the vapor. The exponent q in (2) determines the type of bulk criticality. $q = 1$ describes a noncritical phase. This case has been studied previously in much detail.[5] Within usual Landau theory, $q = 2$ and $q \geq 3$ describe a critical end point and a multicritical end point of higher order. On the other hand, it may also be useful to consider a generalized Landau theory where nonclassical values for the *bulk* exponents can be incorporated. Such generalizations have been studied previously for two problems which are different from, but related to, the problem considered here, namely, (1) for the coexistence of a critical phase and a noncritical one in the infinite bulk system,[15,16] and (2) for the decay of the order parameter profile at bulk criticality in a constrained system.[17,18] In these cases, the effective q value was taken to be

$$2q = 1 + \delta_b , \tag{3}$$

where δ_b is the bulk exponent for the critical isotherm.

The surface or wall potential f_1 in (1) is chosen to be

$$f_1(\phi)=-h_1\phi+\tfrac{1}{2}a_1\phi^2 \ . \qquad (4)$$

For arbitrary values of h_1 and a_1, one finds a complex phase diagram.[19] Here, we will confine our discussion to *critical* depinning which involves two scaling fields and which occurs for $a_1>\bar{a}_1(q)>0$ and for $h_1\to 0^+$. Note that $h_1=0$ corresponds to a finite value of the physical field which couples to the fluid density n since $\phi=(n-n_c)/(n_v-n_c)$.

For the above model, the order parameter profile $M(z)=\langle\phi\rangle$ may be calculated in closed form within Landau theory. The result is[20]

$$M(z)=[\hat{M}^{1-q}+(q-1)u(\hat{l}-z)]^{-1/(q-1)} \ , \qquad (5a)$$

for $0\leqslant z\leqslant\hat{l}$, and

$$M(z)=1-(1-\hat{M})e^{-(z-\hat{l})/\xi} \ , \qquad (5b)$$

for $z\geqslant\hat{l}$. This profile has the shape of a kink with an interface at $z=\hat{l}$. Note that this kink is rather asymmetric since its z dependence is exponential for $z>\hat{l}$ and a power law for $z<\hat{l}$. As $h_1\to 0$, the interface at $z=\hat{l}$ becomes unpinned since

$$\hat{l}\propto h_1^{-\bar{\mu}}, \ \ \bar{\mu}=q-1 \ . \qquad (6)$$

As the interface unbinds, the surface order parameter $M_1\equiv M(z=0)$ goes continuously to zero as

$$M_1=h_1/a_1+O(h_1^q)\propto\hat{l}^{-1/\bar{\mu}} \ . \qquad (7)$$

Note that the (multi-)critical bulk phase corresponds to $M=\langle\phi\rangle=0$. Thus, (7) implies that the *surface layer becomes more and more critical* as the interface moves to infinity. On the other hand, the surface layer is expected to have a large but finite correlation length as long as $\hat{l}$ is still finite. This is indeed the case as will be shown next.

Within Landau theory, the correlation function

$$C(\mathbf{r},zz')=\langle\phi(\mathbf{r},z)\phi(0,z')\rangle_c = \langle\eta(\mathbf{r},z)\eta(0,z')\rangle \ , \qquad (8)$$

with $\eta\equiv\phi-M$, can be expressed by the normal modes of the Gaussian fluctuations. In order to determine these modes, one has to solve the Schrödinger-type equation

$$\left[-\frac{d^2}{dz^2}+f''(M(z))\right]g_n(z)=E_n g_n(z) \qquad (9)$$

[where $f''(x)\equiv d^2f/dx^2$], with the boundary condition

$$\frac{d}{dz}g_n(z)|_0=a_1 g_n(0) \ . \qquad (10)$$

This eigenvalue problem can be solved exactly for all values of q. First, consider $q=2$. In this case, the potential $f''(M(z))$ in (9) reads

$$f''(M(z))=6(1/M_1-z)^{-2}\Theta(\hat{l}-z)+\Theta(z-\hat{l})-\sqrt{5}\delta(z-\hat{l}) \ , \qquad (11)$$

where we have put $u=\xi=1$ for convenience. The eigenmodes $g_n(z)$ are given in terms of the functions $x^{1/2}J_{\pm 5/2}(x)$ where $J_\nu(x)$ are Bessel functions of the first kind[21] and $x=\sqrt{E_n}(1/M_1-z)$. As a result, one finds three different types of modes: (I) *A soft interface mode* $g_0(z)$. Since this eigenmode is the ground state of (9), one has $g_0(z)>0$ for all z. In addition, it is localized around $z=\hat{l}$ and becomes proportional to the zero mode $\dot{M}(z)\equiv dM/dz$ for $h_1\to 0$. The approach towards this limit is, however, subtle, since $g_0(z=0)\propto h_1^3$, whereas $\dot{M}(z=0)\propto h_1^2$. The energy E_0 of this soft mode has the asymptotic behavior

$$E_0=cM_1^5+O(M_1^6)\propto h_1^5 \qquad (12)$$

with $c=30/(4-5\hat{M})$, $\hat{M}=(\sqrt{5}-1)/2$, and M_1 given by (7). (II) *A discrete set of layer modes* $g_n(z)$ with $1\leqslant n\leqslant N$, where N depends on h_1. *Each layer mode* $g_n(z)$ *also becomes soft* for $h_1\to 0$, since its energy goes as

$$E_n=\gamma_n M_1^2-2\gamma_n M_1^3/a_1+O(M_1^4)\propto h_1^2 \ , \qquad (13)$$

with M_1 from (7). $\gamma_n\neq 0$ is determined by $J_{5/2}(\sqrt{\gamma_n})=0$. These eigenfunctions have the asymptotic behavior $g_n(z)\propto h_1^{3/2}$ for fixed $z<<\hat{l}$, $g_n(p\hat{l})\propto h_1^{1/2}$ for $0<p<1$, and $g_n(\hat{l})\propto h_1^{3/2}$. (III) A continuum of *scattering modes* with eigenvalues $E>1$.

As a consequence, the correlation function (8) consists of three parts:

$$C(r,zz')=C_0(r,zz')+C_l(r,zz')+\bar{C}(r,zz') \ . \qquad (14)$$

C_0 and C_l are due to the soft interface mode and to the bunch of soft layer modes, respectively:

$$C_0(r,zz')=\rho^{-(d-3)}\Omega(\sqrt{E_0}\rho)g_0(z)g_0(z') \ , \qquad (15)$$

$$C_l(r,zz')=\rho^{-(d-3)}\sum_{n=1}^{N}\Omega(\sqrt{E_n}\rho)g_n(z)g_n(z') \ , \qquad (16)$$

with

$$\Omega(x)=(2\pi)^{(1-d)/2}x^{(d-3)/2}K_{|d-3|/2}(x)$$

and $\rho=(r^2+\Lambda^{-2})^{1/2}$, where Λ is a high-momentum cutoff for the continuum theory.[23] $\bar{C}$ in (14) is the contribution due to the scattering modes, and is of no interest here. Note that the dependence of the scaling field h_1 enters in (15) and (16) both through E_n and through $g_n(z)$. As a consequence, the asymptotic behavior of $C(r,zz')$ is quite different for different values of z and z'.[19] In the interfacial region, one has $z,z'\simeq\hat{l}$. In this case,

$$C_0(r,\hat{l}\hat{l})\propto r^{1-d/2}\exp(-r/\xi_\parallel) \ , \qquad (17a)$$

$$C_l(r,\hat{l}\hat{l})\propto r^{-d/2}\exp(-r/\xi_l) \ , \qquad (18a)$$

in the limit $r\to\infty$. The two length scales $\xi_\parallel$ and ξ_l are given by

$$\xi_\parallel\equiv E_0^{-1/2}\propto h_1^{-5/2} \ , \qquad (17b)$$

$$\xi_l\equiv E_1^{-1/2}\propto h_1^{-1} \ , \qquad (18b)$$

where (12) and (13) have been used. It follows from (17) and (18) that the asymptotic decay of the correlations in the interfacial region is governed by $\xi_\parallel$ since $\xi_\parallel\sim\xi_l^{5/2}>>\xi_l$.

For general q, (9) can be solved in terms of the functions $x^{1/2}J_{\pm\nu}(x)$ with $\nu=\frac{1}{2}(3q-1)/(q-1)$, $x=\sqrt{E_n}(1/A-z)$, and $A\equiv(q-1)uM_1^{q-1}$. $J_{\pm\nu}(x)$ are again Bessel functions of the first kind.[21] As a result, we obtain the asymptotic behavior

$$\xi_\parallel\propto h_1^{-\bar{\nu}_\parallel}, \ \ \bar{\nu}_\parallel=\tfrac{1}{2}(3q-1) \ , \qquad (19)$$

$$\xi_l\propto h_1^{-\bar{\mu}}, \ \ \bar{\mu}=q-1 \ , \qquad (20)$$

for the two correlation lengths. The detailed behavior of E_n and $g_n(z)$ will be discussed elsewhere.[19]

The above analysis of $C(r,zz')$ implies that the interface fluctuations and the fluctuations within the (almost) critical layer are governed by the two different length scales $\xi_\parallel$ and ξ_l, respectively. Note that the correlation length ξ_l is found to be proportional to the layer thickness $\hat{l}$ as given by (6). As a consequence, the surface layer appears to be a peculiar finite-size system where the "finite size" $\hat{l}$ always matches the correlation length ξ_l.

So far, we have discussed the semi-infinite system *at* the bulk (multi-)critical end point. In this case, the behavior at critical depinning depends only on the scaling field h_1 as discussed above. There is, however, an additional scaling field denoted by t, which governs the approach *towards the (multi-)critical* end point. If this point is approached on some thermodynamic path inside the bulk vapor phase, the potential $f(\phi)$ has the general form $f(\phi)=t+g(\phi,t)$, for $\phi=0$ with $t>0$ and $g(\phi,0)=\frac{1}{2}u^2\phi^{2q}$, as in (2). For such a potential, one finds the following asymptotic behavior from an investigation of Landau theory and Gaussian fluctuations:[19,22]

$$\hat{l}\sim\xi_l\propto t^{-\mu},\quad \mu=\frac{1}{2}-\frac{1}{2q}\ , \tag{21}$$

$$\xi_\parallel\propto t^{-\nu_\parallel},\quad \nu_\parallel=\frac{3}{4}-\frac{1}{4q}\ , \tag{22}$$

$$f_s\propto t^{2-\alpha_s},\quad \alpha_s=\frac{3}{2}-\frac{1}{2q}\ , \tag{23}$$

where f_s denotes the surface free energy. Note that $\mu=\alpha_s-1$ as in all types of depinning transitions studied previously. In addition, $\alpha_s=2\nu_\parallel$. This curious relation also holds in all previous cases for any value of d, as can be seen from Tables 1 and 2 in Ref. 8(b).

The above results clearly show that there are two different types of fluctuations, namely, (1) capillary waves due to the soft interface mode, and (2) critical fluctuations within the surface layer due to the soft layer modes. Both types of fluctuations can affect the results of Landau theory. Some estimate of their relative importance may be obtained if one considers their effects separately.

First, consider the capillary waves which give a Gaussian (or one-loop) contribution

$$\Delta f_s=\int\frac{d^{d-1}q}{(2\pi)^{2-1}}\ln(q^2+E_0)\sim\xi_\parallel^{-(d-1)} \tag{24}$$

to the surface free energy. If one compares (24) to the surface free energy f_s as obtained in Landau theory, one finds the boundary dimension

$$d_\parallel^*(q)=(5q+1)/(3q-1)\ . \tag{25}$$

For $d<d_\parallel^*(q)$, capillary waves become important, and $\xi_\parallel^{-(d-1)}$ is more singular than the Landau f_s.

Due to the presence of capillary waves, there is yet another boundary dimension, namely, $d_r^*=3$. For $d\leq d_r^*$, the interface becomes rough as it unbinds from the surface or wall. The asymptotic behavior of its width $\xi_\perp$ is given by[23]

$$\xi_\perp^2\sim C_0(0,\hat{l}\hat{l})\propto\begin{cases}\ln(\xi_\parallel) & d=3\ ,\\ \xi_\parallel^{3-d} & d<3\ .\end{cases}$$

For $\xi_\perp\sim\hat{l}$, capillary waves are expected to affect the critical behavior. In fact, the relation $\xi_\perp\sim\hat{l}$ again leads to $d=d_\parallel^*$ as given by (25). It will be shown elsewhere[24] that this equivalence is true in general.

The properties of capillary waves can be studied most conveniently in the framework of effective interface potentials $V(l)$ for the fluctuating interface coordinate $l(\mathbf{r})$.[3,6–8] In the present context, the effective potential may be taken as

$$V(l)=tl-h_1l^{-a}+l^{-b}\ , \tag{26}$$

with $a=q/(q-1)$ and $b=(q+1)/(q-1)$, where unimportant constants have been omitted. It is remarkable that this potential contains powers of l, although all interactions are short ranged. If MF theory is applied to (26), one recovers all results of Landau theory for the critical exponents as described above. For $d=2$, transfer matrix methods yield the surface free energy $f_s\propto h_1^{q+1}$ for $q>3$ in accordance with Landau theory. In addition, one finds[19] $f_s\propto h_1^{(2q-2)/(q-2)}$ for $2<q<3$, and $f_s\propto\exp(-2\pi/\delta h_1)$ for $q=2$, with $\delta h_1=h_1-h_1^*$ and $h_1^*=\frac{1}{8}$ for the potential (26).[25]

On the other hand, one may consider the critical layer fluctuations in the absence of capillary waves. Their Gaussian contribution to the surface free energy is

$$\Delta f_s=\int\frac{d^{d-1}q}{(2\pi)^{d-1}}\sum_{n=1}^{N}\ln(q^2+E_n)\ , \tag{27}$$

with $E_n\sim n^2\hat{l}^{-2}\sim n^2\xi_l^{-2}$. To leading order, this is just the Gaussian (or one-loop) contribution to the free energy per unit area for a slab of thickness $\hat{l}$ at bulk criticality. This contribution contains a singular term $\propto\hat{l}\xi_l^{-d}$, which one expects quite generally from finite-size scaling. If one compares this term with the Landau result for the surface free energy, one obtains

$$d_l^*=2q/(q-1)\ . \tag{28}$$

This is just the upper critical dimensions for the *bulk critical behavior*. For instance, $d_l^*=4$ for $q=2$, which corresponds to a bulk critical point.

Some insight into the effects of the critical layer fluctuations on the wetting transitions can be gained by comparison with a similar problem, namely, the decay of the order parameter profile at a bulk critical point in a constrained system.[17,18,26] In this case, Landau theory predicts a decay $\propto z^{-1}$, whereas scaling theory[17,18] and renormalization-group work[26] yield $z^{-\omega}$, with $\omega=\beta_b/\nu_b=(d-2+\eta_b)/2=(2-\eta_b)/(\delta_b-1)$.[27] Since $\omega<1$, the critical fluctuations *suppress* the decay of the order-parameter profile. We expect that the critical layer fluctuations studied here will have a similar effect on the order parameter profile $M(z)$ as given by (5a). Such a change in $M(z)$ will also modify the effective interface potential of (26).

It is possible to extend the above analysis in various ways. First of all, one may depart from the scalar model (1), and consider more general models which involve several physical densities.[28] This would allow a discussion of the critical end points in ^{4}He. In addition, one may include long-range surface or substrate potentials as in Ref. 8(b). Finally, the effects of the critical layer fluctuations on the depinning transition may be systematically studied via a loop expansion for the order parameter profile. Work in these directions is in progress.

We thank D. M. Kroll, H. Wagner, and R. K. P. Zia for helpful discussions.

*Present address: Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, NY 14853.

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